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EXPERIMENTAL ABSORPTION COEFFICIENTS FOR ELEVEN CO LASER LINES

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Ohio State University

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ELEVEN CO LASER LINES

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13. ABSTRACT

This report describes experimental measurements of molecular absorption coefficients for H_2O-N_2 mixtures using a multipass absorption cell and a CO laser source. Eleven highly transmitting CO lines between 1854.933 and 1978.586 cm^{-1} were studied.

Results are compared with synthetic spectrum calculations for three different line shapes.

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KEY WORDS	LINK A		LINK B		LINK C	
	ROLE	AT	ROLE	AT	ROLE	AT
CO laser						
Water vapor						
Molecular absorption						
Laser propagation						
Infrared spectroscopy						
Atmospheric transmittance						

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ELEVEN CO LASER LINES

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FOREWORD

This report, The Ohio State University Research Foundation Report Number 3271-5 (fifth Quarterly Report), was prepared by The Ohio State University ElectroScience Laboratory, Department of Electrical Engineering at Columbus, Ohio. Research was conducted under Contract F30602-72-C-0016. Mr. James W. Cusack, RADC(OCSE), of Rome Air Development Center, Griffiss Air Force Base, New York, is the Project Engineer.

PUBLICATION REVIEW

This technical report has been reviewed and is approved

RADC Project Engineer

ii

TABLE OF CONTENTS

iv

I. INTRODUCTION

This report presents laboratory measurements using a White cell of absorption coefficients in H_2O-N_2 mixtures at a total pressure of 760 torr and 74°F for eleven CO laser lines between 1854.933 and 1978.609 cm^{-1}.

The eleven lines studied were selected from a list of the CO lines in the 1840-1990 cm^{-1} band which were observable in our laboratory electric discharge laser.

The experimental results are compared with calculations using the Calfee-Benedict line data table[1] and two line shapes; a) Lorentz, and b) an empirical wing-enhanced line shape of our own construction[2]. For these "window" lines, the Lorentz shape gives much too low absorption. The Ohio State University line shape gives excellent results for five of the six lines which are most clearly in "windows." For the remaining lines there is still very good improvement over results using the Lorentz shape. For all eleven lines the error between experiment and computation, using the Ohio State University shape, is less than 25 percent.

The original disagreement between computation and experiment may also be partly due to factors other than line shape. This is discussed in a later section of the report.

For these eleven CO lines absorption by other atmospheric constituents is negligible. The absorption coefficients for the CO lines are greater than has been previously determined[3,4] for the 10.6μ P-20 line of the CO_2 laser using a 330 ppm CO_2 plus H_2O-N_2 mixture, except for the 1978.609 cm^{-1} line at water vapor pressures of less than 3 torr.

II. THE MULTIPASS ABSORPTION CELL

The absorption cell[5] uses a White-type multipass optical system[6] to achieve path lengths of up to one km. Longer paths are possible but have not been necessary in the studies to date.

The cell is 0.607 m in diameter and 16.15 m long. The sample volume is 4.7 m^3. The cell walls were honed smooth during construction in order to reduce water vapor adsorption effects. The optical system consists of a mirror 30.48 cm in diameter and a 50.8 cm diameter mirror which is split into two halves which are adjustable in order to change the number of traversals. The mirrors are separated by their common radius of curvature (15.24 m). A six inch diffusion pump and a 100

1

cfm mechanical pump can evacuate the cell to 10^{-5} torr if required. In the measurements described in this report the diffusion pump was not used. Figure 1 shows a picture of the multipass cell.

Distilled water was placed in a glass bottle connected to the absorption cell by rubber vacuum tubing. The water bottle was first connected to a vacuum pump and allowed to outgas before opening the valve to the cell inlet manifold. The cell was allowed to fill as the water in the container vaporized at room temperature. This was a slow process with six to seven hours being required to reach the highest partial pressures (15 torr). Heating the water to increase the vaporization rate increases the danger of condensation and was therefore avoided.

The pressure of the pure water vapor sample was measured with a Roger Gilmont Instruments Model 906 Mercury Micrometric Manometer. This instrument covers the range 0 to 2 inches Hg, with 0.002 inch divisions and can be read to .001 inches. In order to avoid any possibility of a gross reading error the water vapor pressure was also read with a Type 530 Alphatron ® radium ionization gauge. The Alphatron ® and the manometer would differ by 10 to 15 percent due presumably to the lack of a recent calibration of the Alphatron ® . The manometer readings were used and reproducibility of a manometer measurement was better than .03 torr.

After filling with water vapor to the desired pressure, nitrogen was added to bring the total pressure to 760 torr as read on a one-meter long U-tube manometer. Then fans in the absorption cell were turned on to mix the gases for approximately twelve hours. One to two hours after the fans were turned off the measurements of transmission could begin. This time was allowed for gas stabilization.

The dew point of the water vapor-air mixture was measured with a condensation type hygrometer (Cambridge Systems Model 880). In a typical measurement the manometer indicated 6.1 torr water vapor before the nitrogen was added and the dew point of the mixture after twelve hours was 41.5°F corresponding to 6.7 torr water vapor. Continued measurement of the dew point over a three day period indicated no change in dew point within the instrument resolution (0.25°F) which was taken as an indication that adsorption effects were unimportant.

The number of cell traversals was determined using a He-Ne laser which was aligned to be coincident with the CO laser beam. Figure 2 shows the optical ray diagram for the White cell.

The number of traversals of the White cell equals 2n+2 where n is the number of images observed on the 30.5 cm mirror. Also note in Fig. 2 that this mirror has cut outs to facilitate the entry and exit of the laser beam. A window is conveniently placed near the 30.5 cm mirror to permit counting of the images.
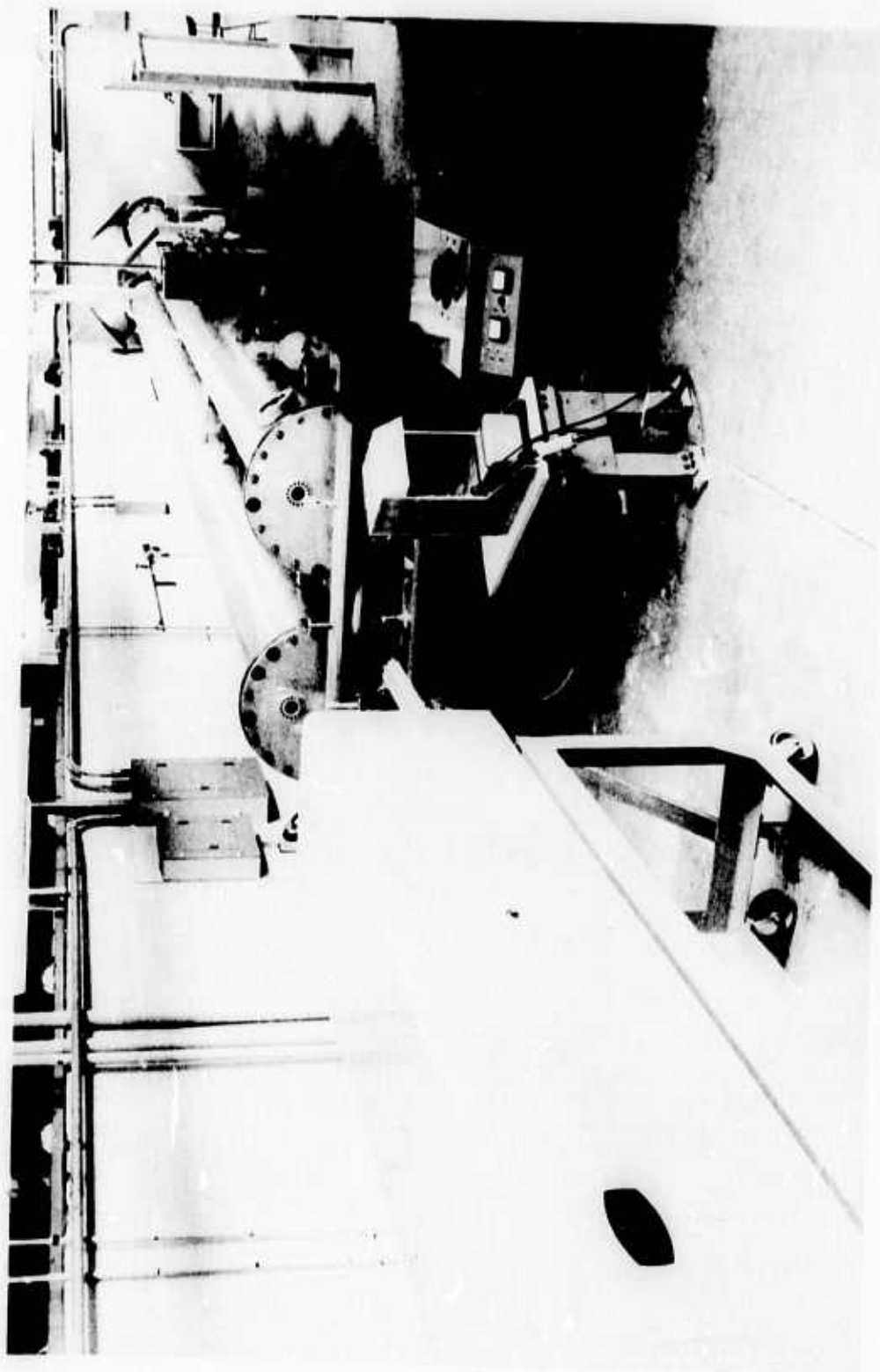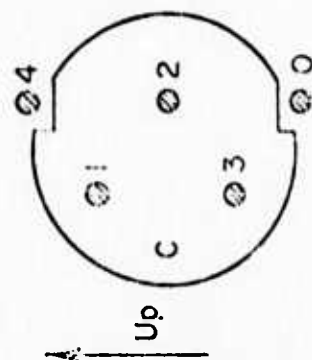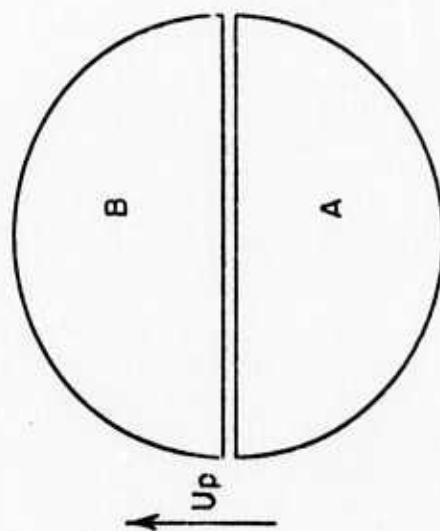
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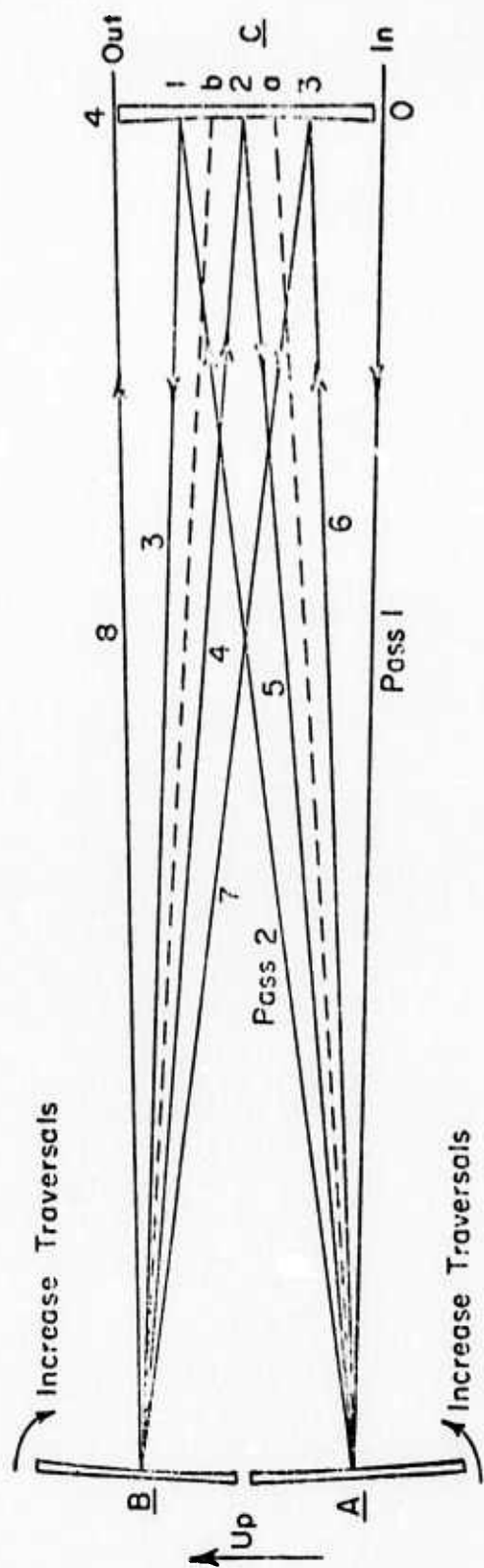Fig. 1. Photograph of White cell.
(circa 1962)

3

Fig. 2. Ray diagram of White cell.

4

Assuming all three mirrors to be identical, the reflectivity of the mirrors was measured, at 5μ, using the CO laser, to be 0.971 ± .001. For a White cell the total number of mirror reflections is $2n+1$ where again n is the number of images on the 30.5 cm mirror. Most of the measurements in the current study were made at a path length of 0.7317 km or 48 traversals. Thus the transmittance of the evacuated cell was $(0.971)^{47} = .25$ due to mirror losses. Entrance and exit window reflection losses reduced the effective transmittance to 0.22 for the 48 traversal path. The entrance and exit windows are un-coated calcium fluoride flats approximately 0.23 inches (5.8 mm) thick. Due to the more than adequate CO laser power, the cell loss was not a problem in these studies.

Another potential problem with multipass cells is that very small changes in mirror reflectivity, if present, could result in large changes in measured transmittance. Burch[7] was concerned that condensation on the mirror surfaces could result in reflectivity changes. He conceived a special optical system which doubled the number of mirror reflections but did not increase the path length but found no evidence of transmittance changes. We have examined our results and have also concluded that this was not a problem in our studies.

The accuracy of the absorption coefficient derived from a White cell transmittance measurement depends on the value of the trans-mittance. Thus when investigating high transmittance window fre-quencies, a very long path length may be required. This problem ultimately limits the usefulness of the White cell as has recently been discussed by Trusty[8] in connection with a study of the laser irradi-ated spectrophone. Figure 3, from Trusty, gives the absorption coefficient error-multiplication factor versus the transmittance. At 90% transmittance the error factor is approximately ten. Thus if the transmittance can be measured to an accuracy of one percent, the absorption coefficient is known only to 10%. Uncertainties in the transmittance can be reduced by the usual methods of repeated measure-ments of the same quantity, however the basic limitations described above still exist. We have in these studies made repeated measurements of the transmittances at each water vapor pressure. Measurements were also made at thirteen different water vapor pressures and a least square curve fit used to determine the transmittance versus pressure function which would be the basis of the absorption coefficient data. Further error analysis is given in the section describing the measured data.
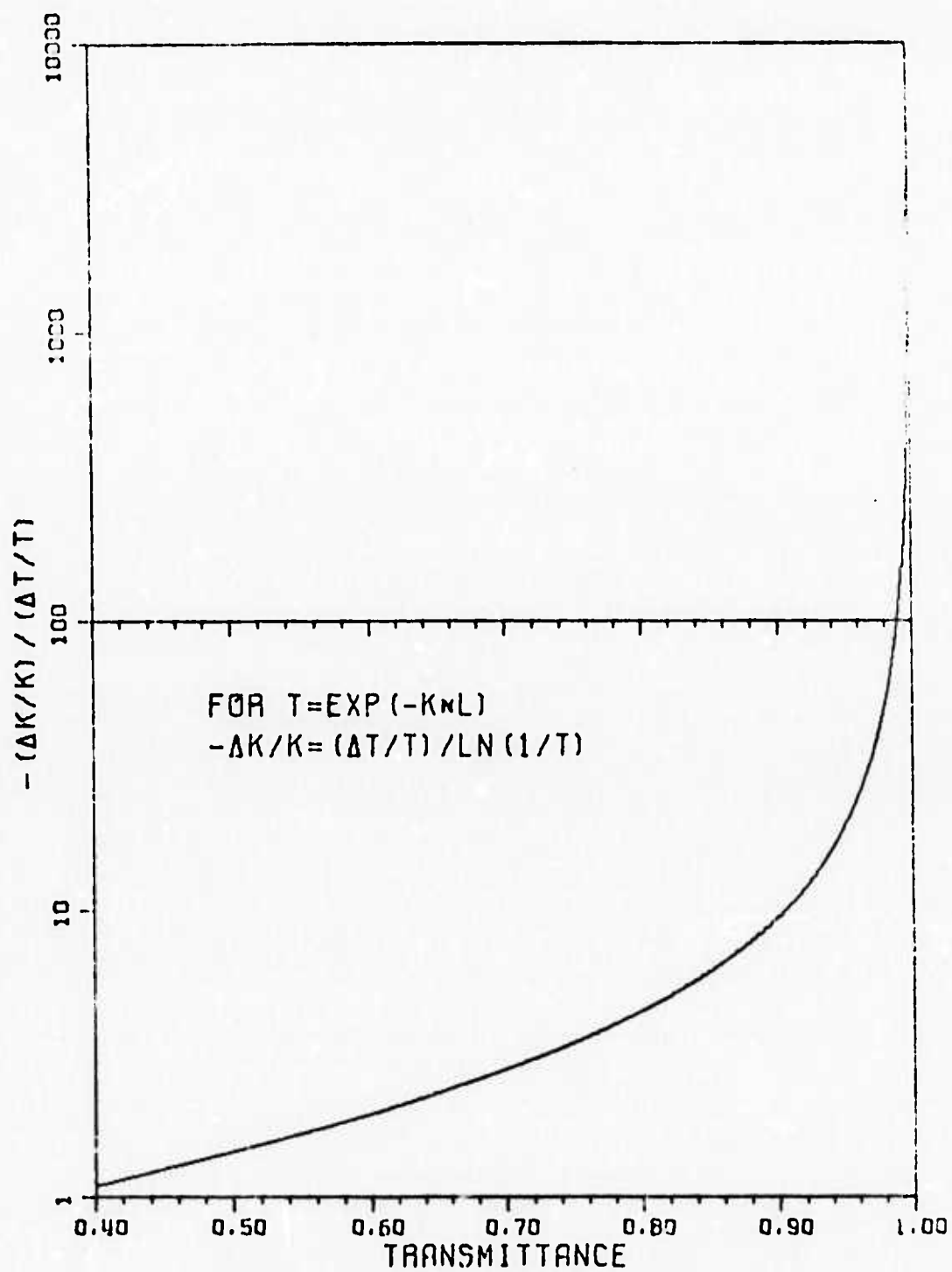
5

Fig. 3. Error multiplication factor versus transmittance for error in absorption coefficient.

6

III. THE CO LASER AND LINE SELECTION

The CO laser source used for these measurements was of a sealed-off highly stabilized design and used a grating and a piezoelectric end mirror drive in order to achieve single line operation. The laser was designed by Dr. Charles Freed[9] and was furnished to the ElectroScience Laboratory by MIT Lincoln Laboratory. Figure 4 shows the laser lines available from this laser when operated at -84°C. Lines closer than 1-2 cm^{-1} can not normally be completely separated. Suitable fine adjustment of grating angle and end mirror position can sometimes be used to enhance one of the blended lines. However, for the measurements reported here only unblended lines were selected.

As a further aid in the selection of the lines to be studied a calculation was made using the Benedict-Calfee water vapor line data tables[10]. The atmospheric model was 5.8 torr water vapor, 760 torr total pressure and 296°K temperature. For this calculation a Lorentz line shape and "conventional" values for the broadening coefficient and BOUND were used[11]. The validity of these assumptions are discussed further in a later section of this report. The equation used was:

$$(1) \qquad -\ln T = \sum_i \frac{S_{oi}\left(\frac{T_o}{T}\right)^{1.5} \exp\left(\frac{-E_i''}{.6951} \cdot \frac{T_o - T}{T_o T}\right) \cdot \alpha_{oi} \, P_e\left(\frac{T_o}{T}\right)^{.62} \cdot u}{\pi\left[(\nu - \nu_{oi})^2 + \alpha_{oi}^2 \, P_e^2 \left(\frac{T_o}{T}\right)^{1.24}\right]}$$

where

$$P_e = \frac{P + 4p}{760} \text{ atm}$$

$$u = \frac{.0288 \, p\ell}{T_o} \text{ pr-cm}$$

α_o = Lorentz half-width in cm^{-1}/atm at STP

S_{oi} = Lorentz line strength at STP

E_i'' = lower energy level in cm^{-1} .

A further discussion of units can be found in reference [11].

Figures 5, 6, and 7 show the synthetic spectra computed over the 1840-1990 cm^{-1} range using the above atmospheric model and a broadening coefficient of 5 and a BOUND of 25. The only significance
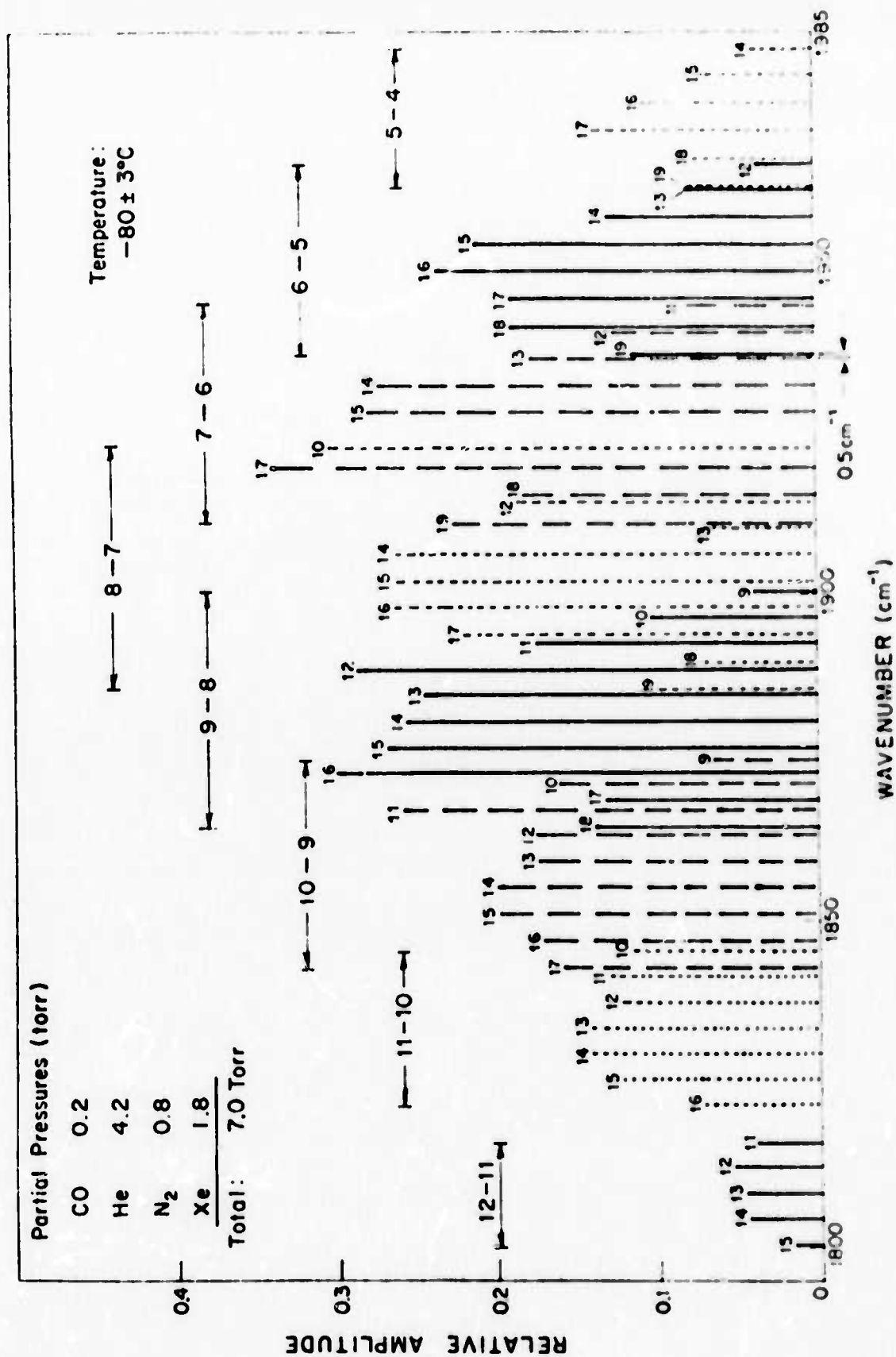
7

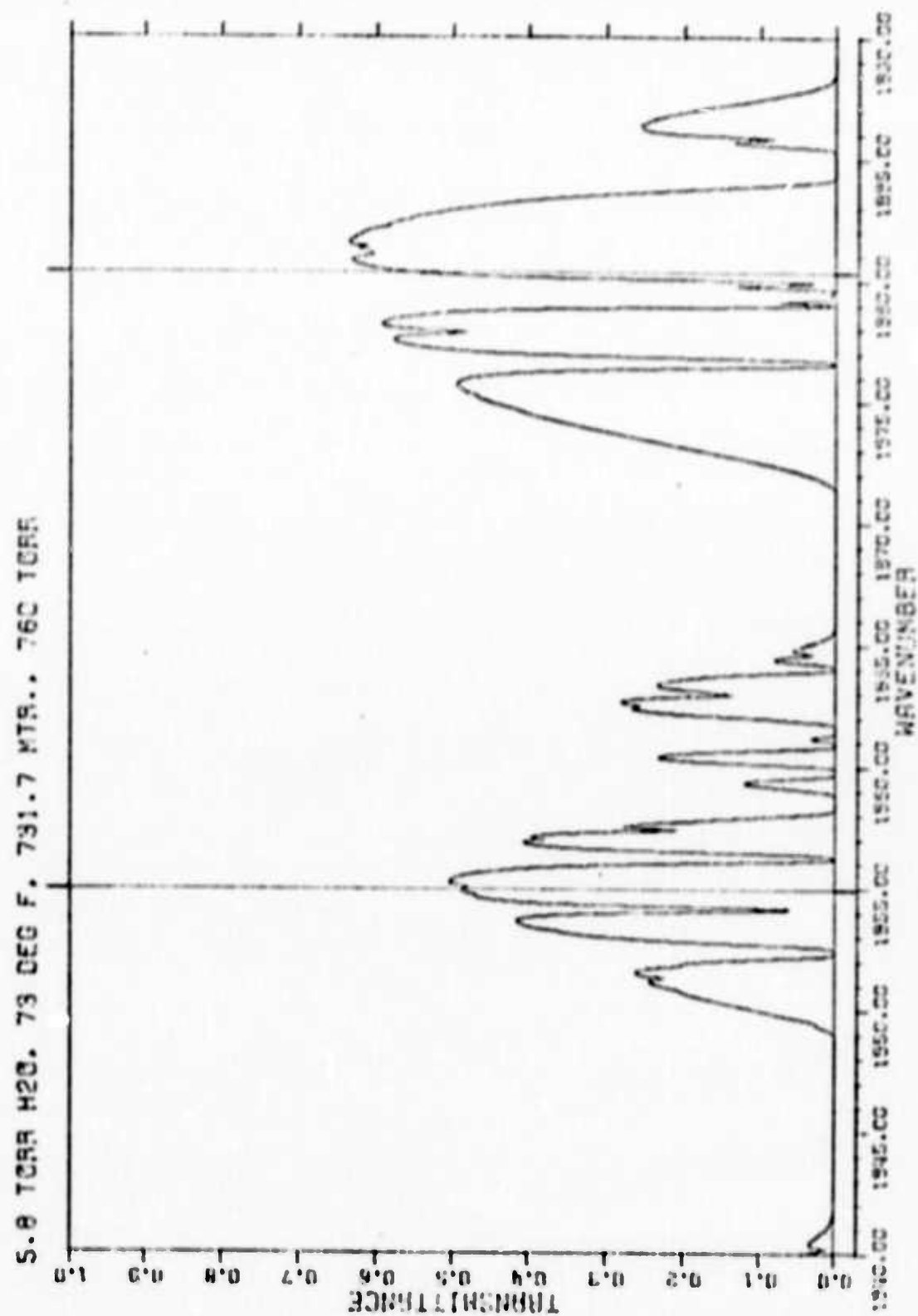Fig. 4. CO laser lines (courtesy Charles Freed).

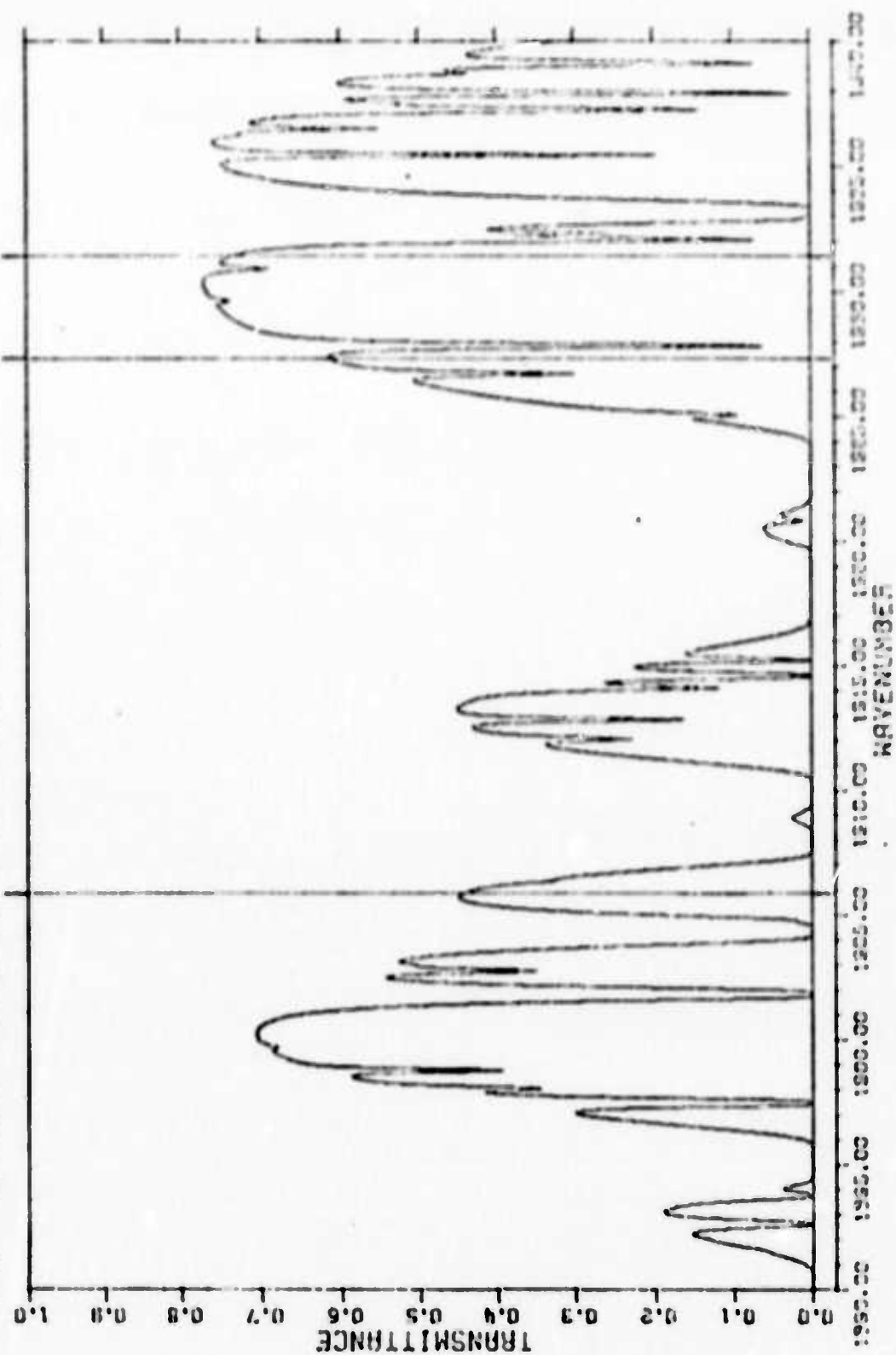Fig. 5. Synthetic spectrum, 1940-1890 cm^{-1}.

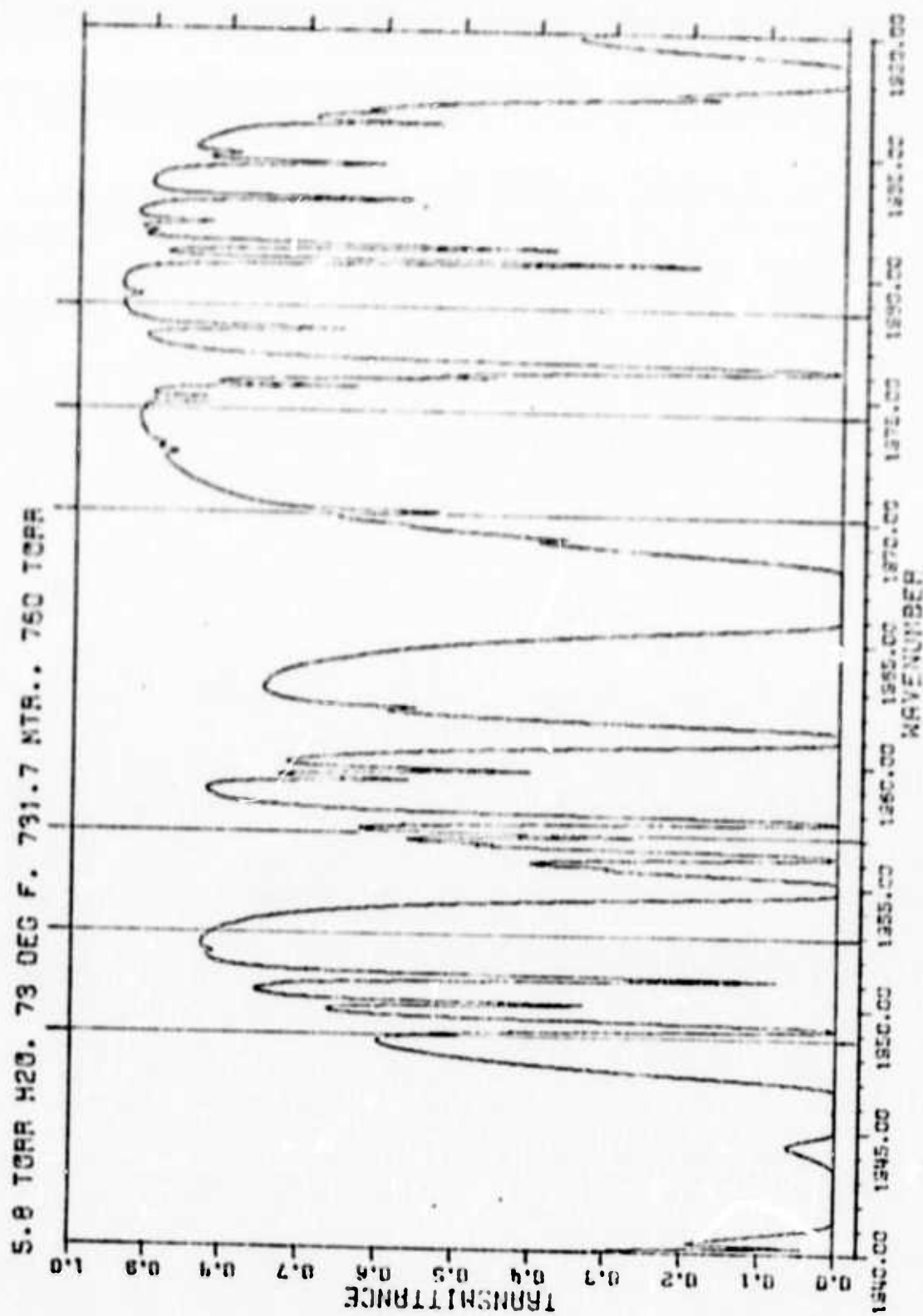Fig. 6. Synthetic spectrum, 1890-1940 cm⁻¹.

10

Fig. 7. Synthetic spectrum, 1940-1990 cm^{-1}.

11

of 5.8 torr is that it was the pressure used in one of the early experimental runs. It corresponds to 28 relative humidity at 73.4°F (23°C). In a later section of this report similar plots expanded in the region of each laser line are presented.

Table I gives the calculated extinction coefficients for each of the 53 CO laser lines observable in the Freed laser between 1837 and 1990 cm^{-1} for the same conditions as Figs. 5-7. The wave numbers of the CO lines were computed using the latest molecular constants by Rao et.al.[12,13] and are believed accurate to ·.002 cm^{-1}.

After comparing the lines available from the laser with the calculated absorption coefficients, eleven lines were selected for experimental study. The lines having the highest predicted transmittance which were unblended in our laser output were selected. They were lines 1,2,4,6,8,9,10,11,12,13, and 18 of Table I. These eleven lines are also marked on Figs. 5, 6, and 7.

IV.   EXPERIMENTAL EQUIPMENT

Figure 8 shows a block diagram of the experimental arrangement. In addition to the absorption cell three focusing mirrors were used. They were selected from available laboratory supplies. The overall optical design was accomplished with the aid of a laser optics computer-aided-design program. The most satisfactory detectors were found to be Eppley Laboratories air-cooled laboratory eight junction bismuth-silver thermopiles. The large size of these detectors (9.52 mm diameter) was found to be an aid in maintaining alignment. The 1/e spot size of the assumed Gaussian beam was computed to be 3.25 mm at the reference detector and 3.9 mm at the signal detector.

The length of the laboratory-air path traversed by the reference beam was only 0.09 meters longer than that of the signal beam path. Thus, even for the most highly absorbing lines and assuming drastic variations in laboratory humidity during the course of a measurement, the error caused by external path difference is entirely negligible.

As far as the absorption cell is concerned the focused spot size in the plane of the 30.5 cm mirror was 0.6 mm and the spot size on the adjustable mirrors was 20 cm.

The optical elements were carefully adjusted until the He-Ne and the CO laser spots were coincident throughout the system. The infrared output signal from the absorption cell was still sufficiently intense to be observable using Optical Engineering, Inc. Model 23 thermal imaging plates. It was found that the optical alignment had to be performed with great care in order to obtain a high degree of reproducibility in the measurements.

12

TABLE I
PREDICTED TRANSMITTANCES FOR 53 CO LINES

T = 73.4   5.8 TORR   760 TORR
LORENTZ LINE SHAPE   B=5   BOUND=25

RANK		IDEN.		K (km⁻¹)	WAVE NUMBER (cm⁻¹)
1	x	5 – 4	15	0.085	1978.586
2	x	5 – 4	16	0.130	1974.374
3		5 – 4	14	0.157	1982.766
4	x	6 – 5	15	0.286	1952.907
5		6 – 5	19	0.383	1936.001
6	x	7 – 6	14	0.426	1931.409
7		9 – 8	9	0.479	1900.049
8	x	5 – 4	17	0.626	1970.129
9	x	7 – 6	15	0.672	1927.299
10	x	6 – 5	16	0.761	1948.729
11	x	9 – 8	14	0.807	1880.348
12	x	10 – 9	14	0.985	1854.933
13	x	8 – 7	14	1.112	1905.841
14		7 – 6	13	1.136	1935.486
15		7 – 6	12	1.151	1939.529
16		10 – 9	9	1.274	1874.459
17		8 – 7	12	1.404	1913.891
18	x	6 – 5	14	1.449	1957.051
19		9 – 8	15	1.546	1876.309
20		6 – 5	12	1.581	1965.242
21		10 – 9	12	1.985	1862.843
22		8 – 7	16	2.017	1897.659
23		10 – 9	15	2.045	1850.928
24		7 – 6	18	2.548	1914.774
25		9 – 8	11	2.586	1892.269
26		8 – 7	17	3.042	1893.519

13

TABLE I (Contd.)

T = 73.4   5.8 TORR   760 TORR
LORENTZ LINE SHAPE   B = 5   BOUND = 25

| RANK	IDEN		K (km⁻¹)	WAVE NUMBER (cm⁻¹)
27	5 - 4	19	3.174	1961.541
28	9 - 8	16	3.778	1872.236
29	6 - 5	17	3.864	1944.519
30	6 - 5	18	4.122	1940.276
31	9 - 8	10	4.254	1896.176
32	5 - 4	18	6.597	1965.851
33	10 - 9	13	7.732	1858.904
34	11 - 10	11	7.756	1841.306
35	9 - 8	12	8.334	1888.329
36	7 - 6	19	8.619	1910.534
37	7 - 6	11	8.920	1943.540
38	9 - 8	18	13.149	1863.993
39	8 - 7	10	13.526	1921.809
40	8 - 7	19	13.926	1885.141
41	10 - 9	16	14.418	1846.891
42	7 - 6	17	15.512	1918.982
43	9 - 8	13	22.085	1884.355
44	8 - 7	15	22.125	1901.766
45	10 - 9	17	26.402	1842.821
46	10 - 9	11	32.659	1866.748
47	10 - 9	10	36.277	1870.620
48	6 - 5	13	55.313	1961.163
49	11 - 10	10	69.346	1845.143
50	11 - 10	12	79.099	1837.436
51	9 - 8	17	194.671	1868.131
52	8 - 7	18	204.650	1889.346
53	8 - 7	13	237.425	1909.883

14
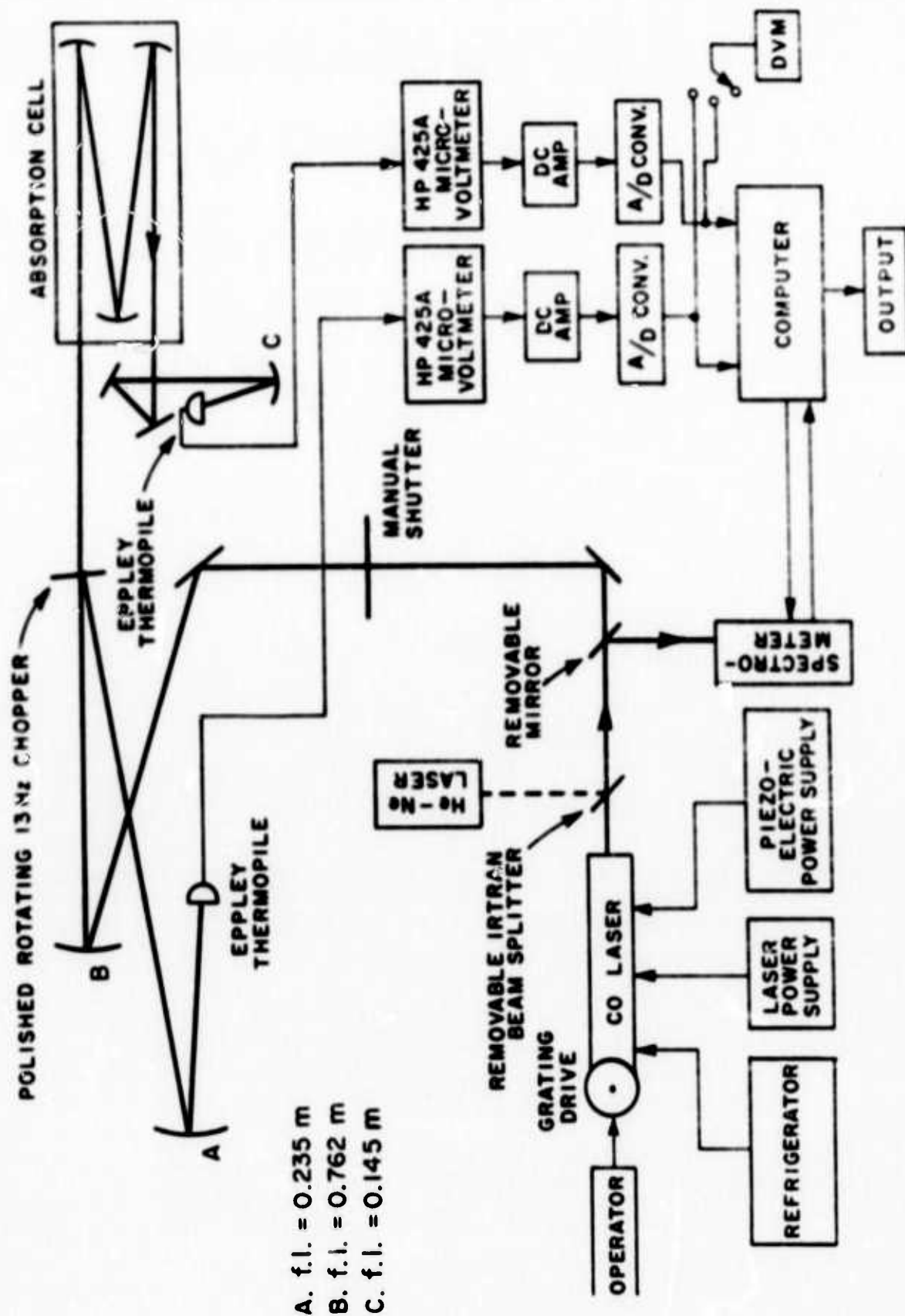
Fig. 8. Diagram of laser absorption experiment.

15

As a result of previous experience no beamsplitters were used. Instead the reference signal was obtained by reflection from the surface of a semi-circular polished 13 Hz chopper made of sheet aluminum.

The detector signals were amplified by HP425A microvoltmeters whose output was further amplified to the 10 volt level by standard data amplifiers, which were connected to separate channels of a 14 bit A/D converter and an SDS-920 laboratory computer. The DVM was used as a convenient aid during optical alignment. The manual shutter was used to block the laser beam so that the computer program could record the amplifier zero levels.

The automatic data recording system in addition to increasing the reproducibility of the measurements was a great convenience.

For a given laser line the reference and signal detector voltages were each read 100 times 50 msec apart. Then the rms deviations and the ratio of the signals was computed. The large number of samples reduced the rms deviation and increased its reproducibility. The above cycle was repeated three times and the average of the three ratios was used to obtain the final value.

The transmittance (uncorrected) is the quotient of the ratio obtained with the atmospheric sample in the cell to that observed with the cell evacuated. A refined value was obtained from the data reduction program which will be described later. Table II gives a schematic diagram which describes the operation of the data-taking program.

A background, i.e., cell evacuated, ratio was obtained both before and after the sample measurement. As indicated earlier eight to twenty-four hours elapsed between the first background and the sample measurement to allow for mixing of the sample gases. The second background was usually obtained within one hour of the sample measurement.

There was always some difficulty in reproducing the before and after background ratios with the percent difference varying from 0.1 to 3.9 percent. Careful experimental technique reduced the variation somewhat but generally the variation was random. In data reduction the average of the two background ratios was used.

The linearity of the amplifier - A/D converter chain was carefully measured using an Analogic AN3100 secondary DC voltage standard as a signal source. The deviations from linearity were found to be negligible.

16

TABLE II
FLOW CHART OF DATA RECORDING PROGRAM

17
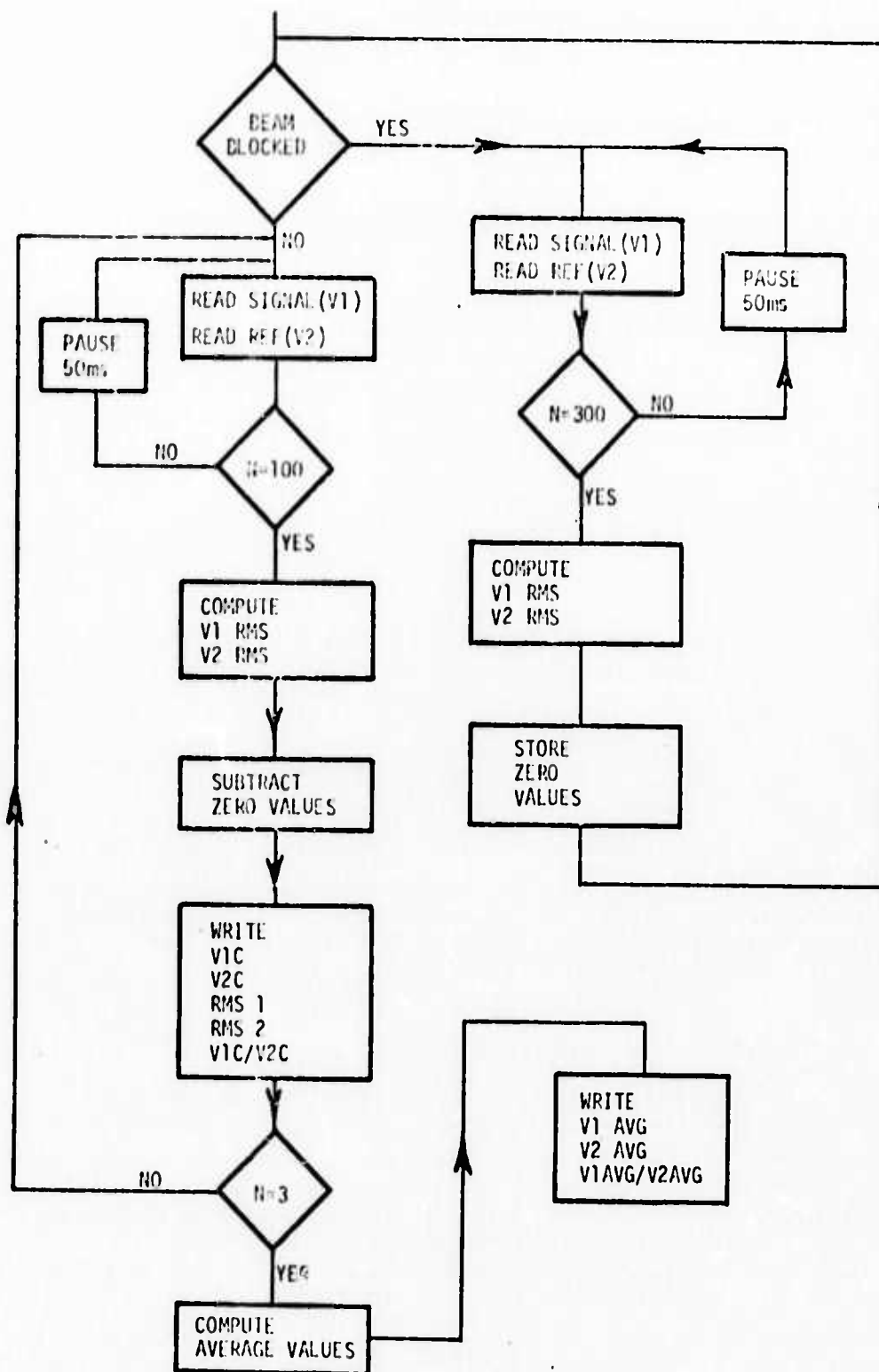
It was necessary to record the HP425A voltmeter scale used for the reference and signal channels. Also it was necessary to use the same scales during the sample measurement as were used during the background measurement.

Absolute calibrations of voltage versus power were available for the Eppley thermopiles. Sufficient data was now available so that one could correct for the effect of detector non-linearity. Three Eppley detectors were available which had been factory calibrated over different but overlapping ranges. Using a variable aperture chopper placed before the CO laser as an adjustable attenuator, the three thermopiles were intercompared and calibrated over the range one to forty-five milliwatts. A least square polynomial curve fit routine was used to obtain the coefficients of quadratic voltage versus power expressions for each of the detectors.

Calibration factors were determined which permitted conversion of the A/D converter readings to absolute millivolts at the detector. Table III is a schematic diagram of the data reduction program which produces the final plots of absorption coefficient versus water vapor partial pressure for each laser line, fully corrected for detector non-linearities and with data points at each water vapor pressure least square fit to $K = bp + cp^2$. Note that in any procedure which fits an equation to data the experimenter must first select the form of the equation to be used. In the next section the reasons for the selection of the above equation are explained.
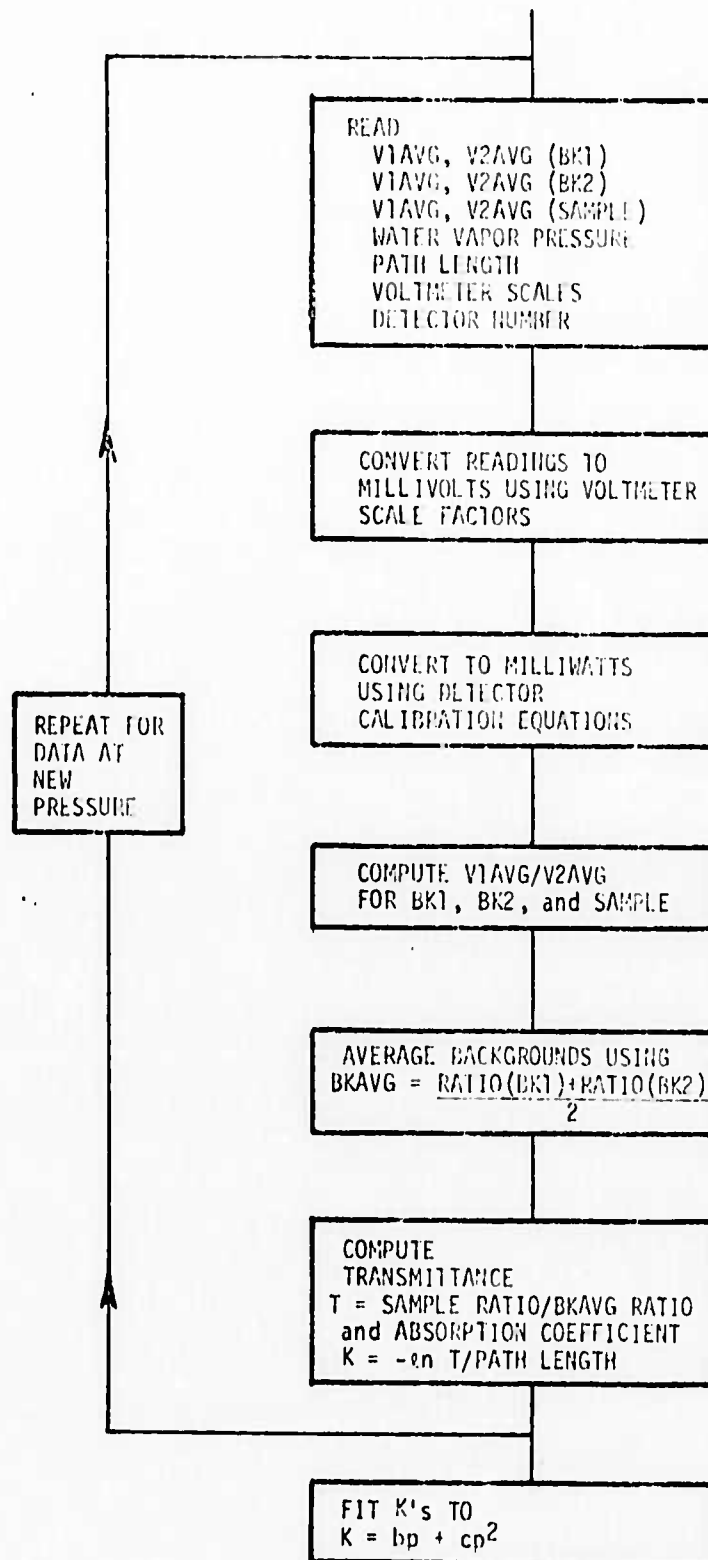

V. MEASURED ABSORPTION COEFFICIENTS

Figures 9-19 present the measured absorption coefficients for the eleven laser lines as a function of the water vapor partial pressure. All measurements were made at approximately 74°F and a total pressure of 760 torr. Nitrogen was the broadening gas in all cases. Table IV presents the same results in a tabular form.

For the curve fitting routine it was decided to fit to $K = bp + cp^2$ rather than $K = a + bp + cp^2$ for the following reasons. This curve would of necessity, pass through the origin as it should and, most importantly, it permitted a simple interpretation in terms of a self-broadening coefficient as will now be described. The alternate procedure of fitting to $a + bp + cp^2$ was also carried out. It was noted that the curves still came near to the origin, an additional indication that the overall accuracy of the data was good.

If a Lorentz line shape is assumed and if a frequency in the wings of all lines is considered, we have

18

TABLE III
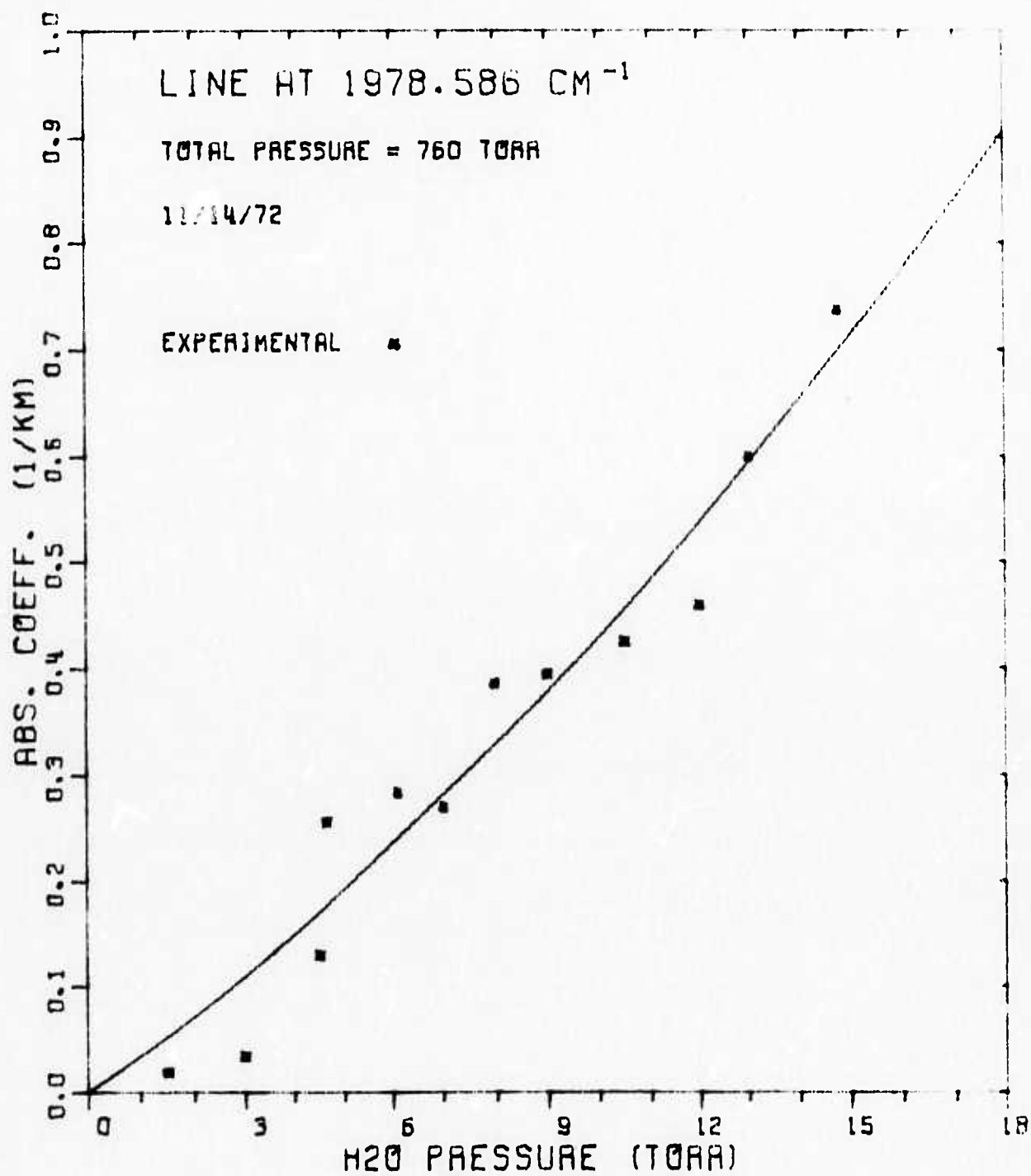## FLOW CHART OF DATA REDUCTION PROGRAM

```
                    ┌──────────────────────────────┐
                    │ READ                         │
                    │   V1AVG, V2AVG (BK1)         │
                    │   V1AVG, V2AVG (BK2)         │
                    │   V1AVG, V2AVG (SAMPLE)      │
                    │   WATER VAPOR PRESSURE       │
                    │   PATH LENGTH                │
                    │   VOLTMETER SCALES           │
                    │   DETECTOR NUMBER            │
                    └──────────────────────────────┘
                                  │
                    ┌──────────────────────────────┐
                    │ CONVERT READINGS TO          │
                    │ MILLIVOLTS USING VOLTMETER   │
                    │ SCALE FACTORS                │
                    └──────────────────────────────┘
                                  │
       ┌──────────┐   ┌──────────────────────────────┐
       │ REPEAT FOR│   │ CONVERT TO MILLIWATTS        │
       │ DATA AT   │   │ USING DETECTOR               │
       │ NEW       │   │ CALIBRATION EQUATIONS        │
       │ PRESSURE  │   └──────────────────────────────┘
       └──────────┘                │
                    ┌──────────────────────────────┐
                    │ COMPUTE V1AVG/V2AVG          │
                    │ FOR BK1, BK2, and SAMPLE     │
                    └──────────────────────────────┘
                                  │
                    ┌──────────────────────────────┐
                    │ AVERAGE BACKGROUNDS USING    │
                    │ BKAVG = RATIO(BK1)+RATIO(BK2)│
                    │                  2           │
                    └──────────────────────────────┘
                                  │
                    ┌──────────────────────────────┐
                    │ COMPUTE                      │
                    │ TRANSMITTANCE                │
                    │ T = SAMPLE RATIO/BKAVG RATIO │
                    │ and ABSORPTION COEFFICIENT   │
                    │ K = -ℓn T/PATH LENGTH        │
                    └──────────────────────────────┘
                                  │
                    ┌──────────────────────────────┐
                    │ FIT K's TO                   │
                    │ K = bp + cp²                 │
                    └──────────────────────────────┘
```

AVERAGE BACKGROUNDS USING
$$BKAVG = \frac{RATIO(BK1)+RATIO(BK2)}{2}$$

COMPUTE TRANSMITTANCE
T = SAMPLE RATIO/BKAVG RATIO
and ABSORPTION COEFFICIENT
$K = -\ell n\ T/$PATH LENGTH

FIT K's TO
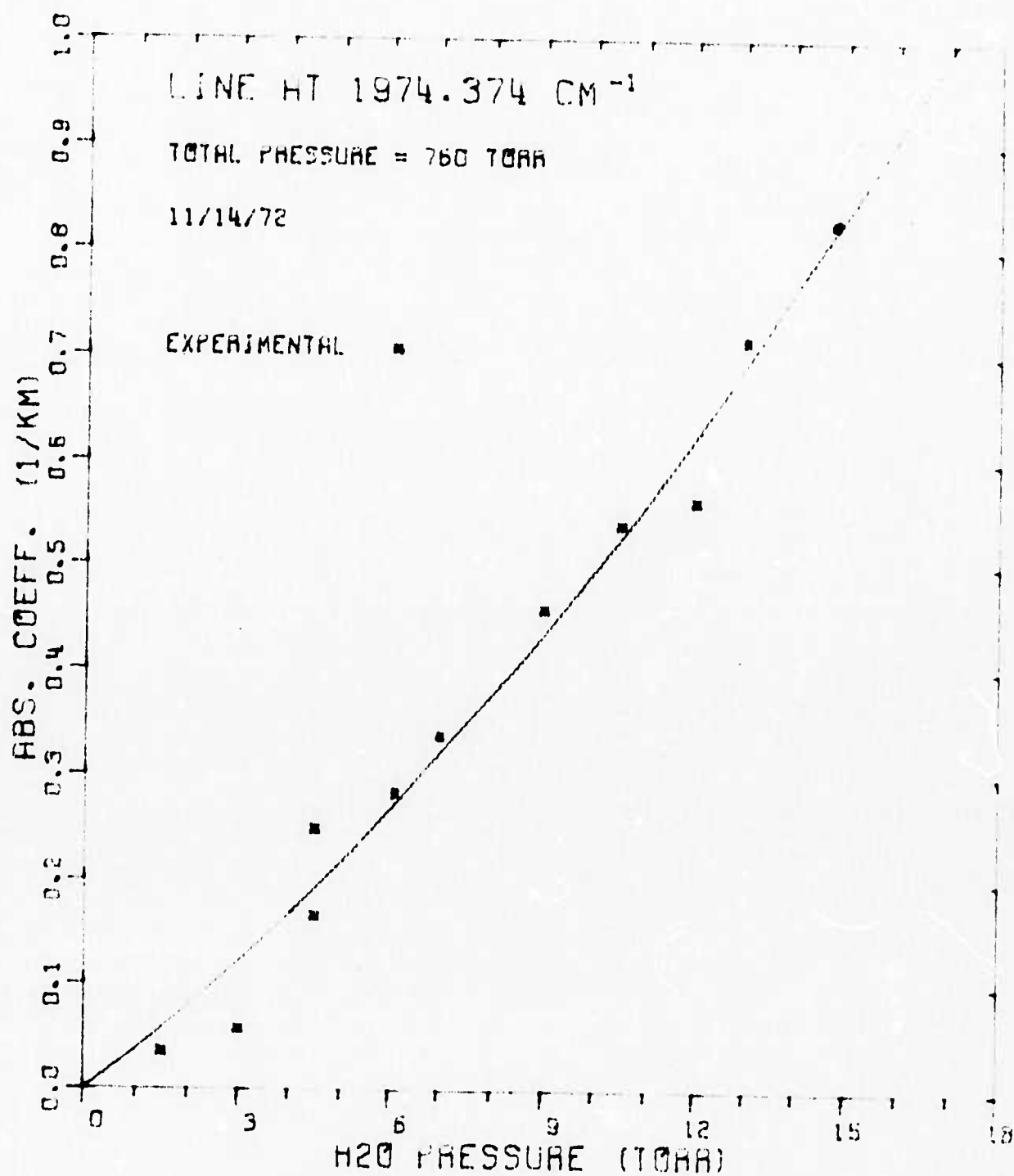$K = bp + cp^2$

19

Fig. 9. Experimental data, 1978.586 cm^{-1}.
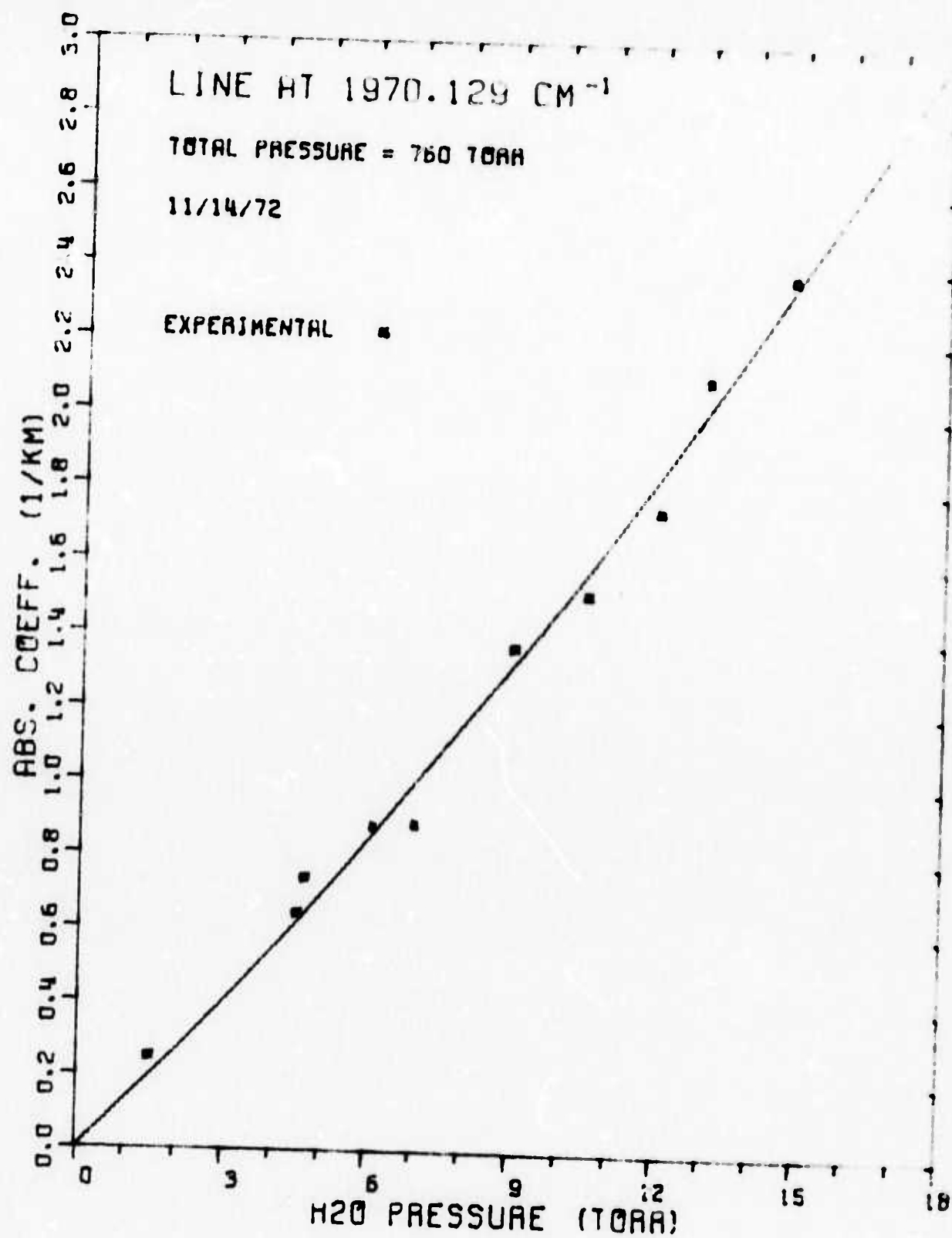
20

Fig. 10. Experimental data, 1974.374 cm⁻¹.
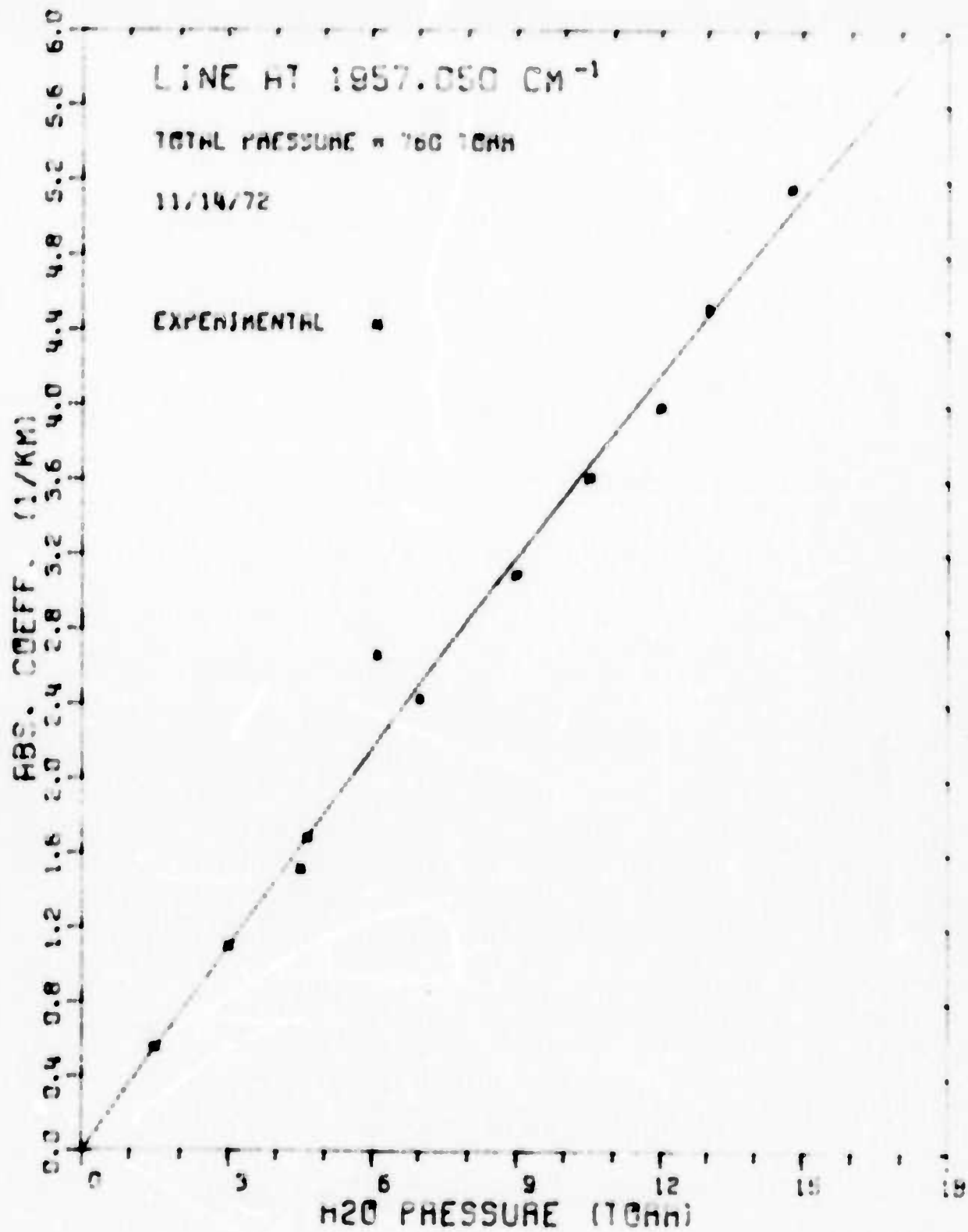
21

Fig. 11. Experimental data, 1970.129 cm⁻¹.

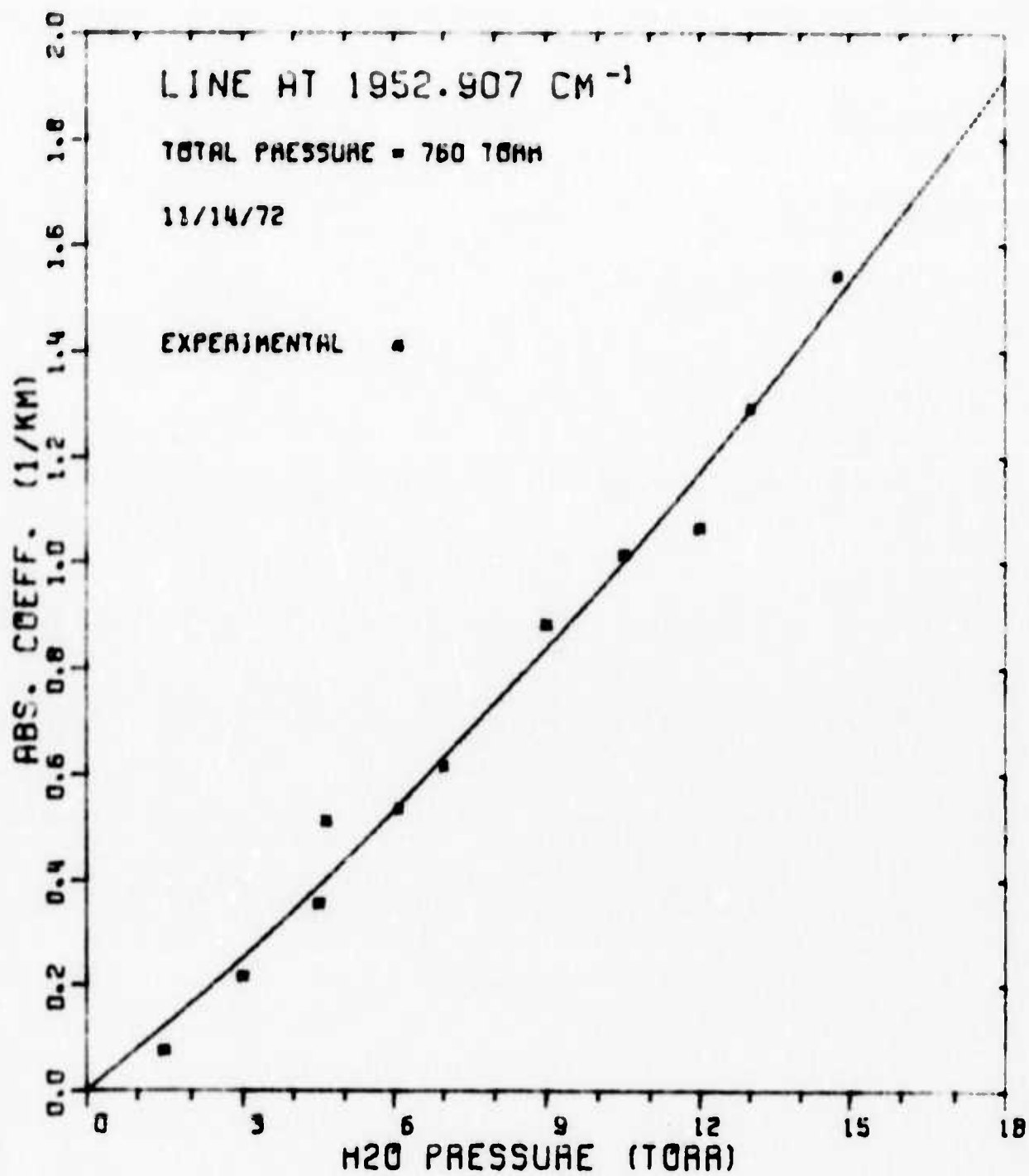Fig. 12. Experimental data, 1957.050 cm⁻¹.

23

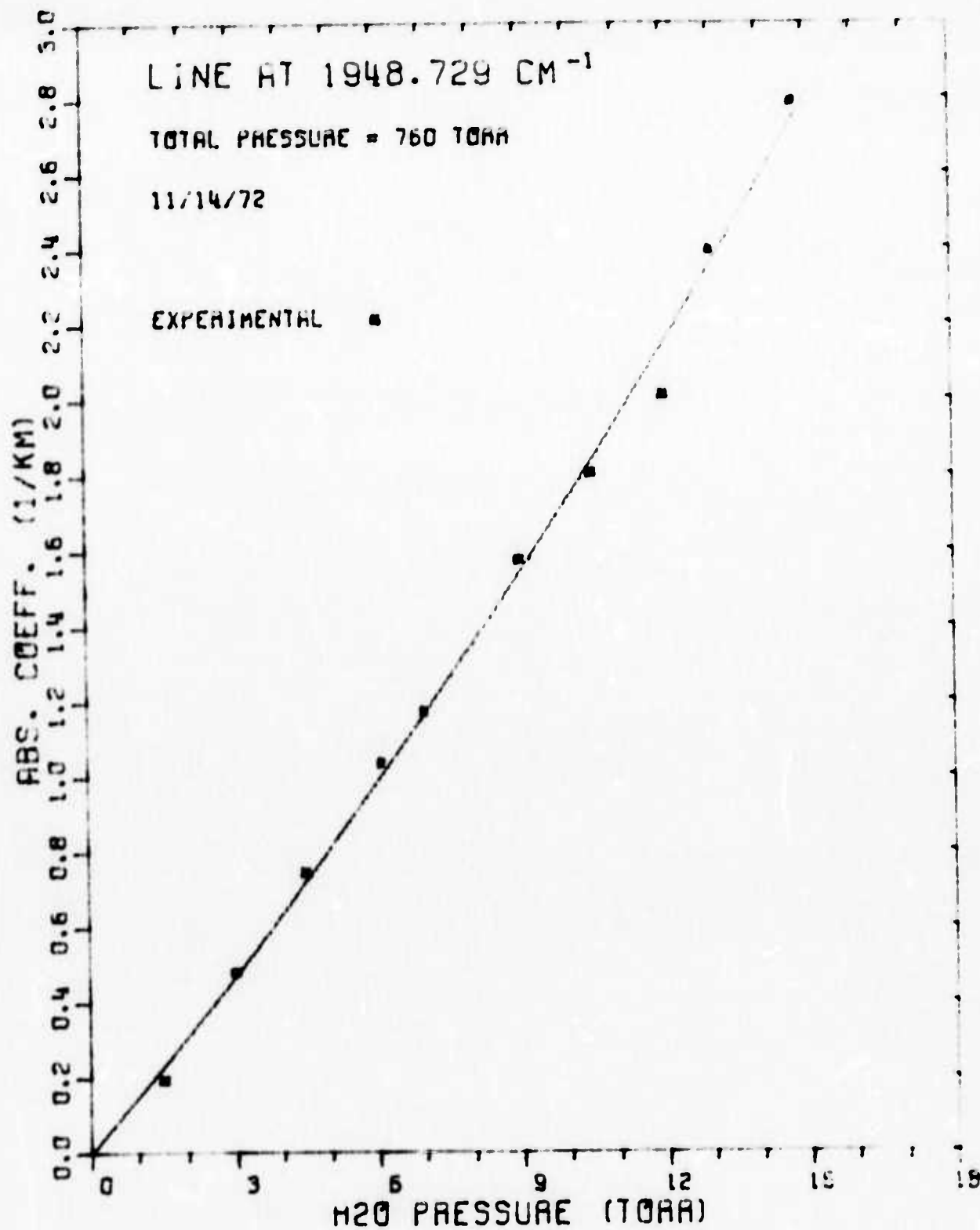Fig. 13. Experimental data, 1952.907 cm^{-1}.

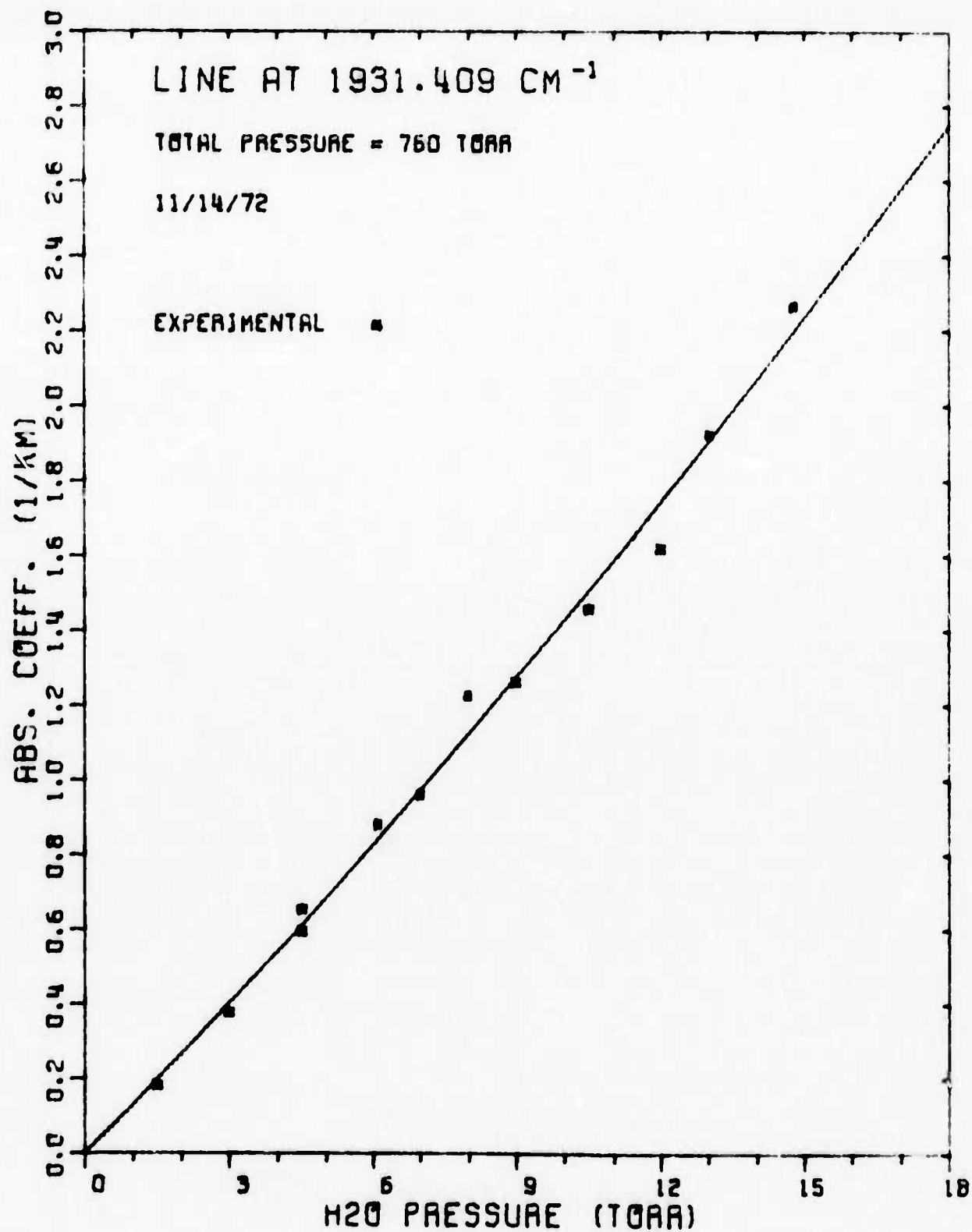Fig. 14. Experimental data, 1948.729 cm^{-1}.
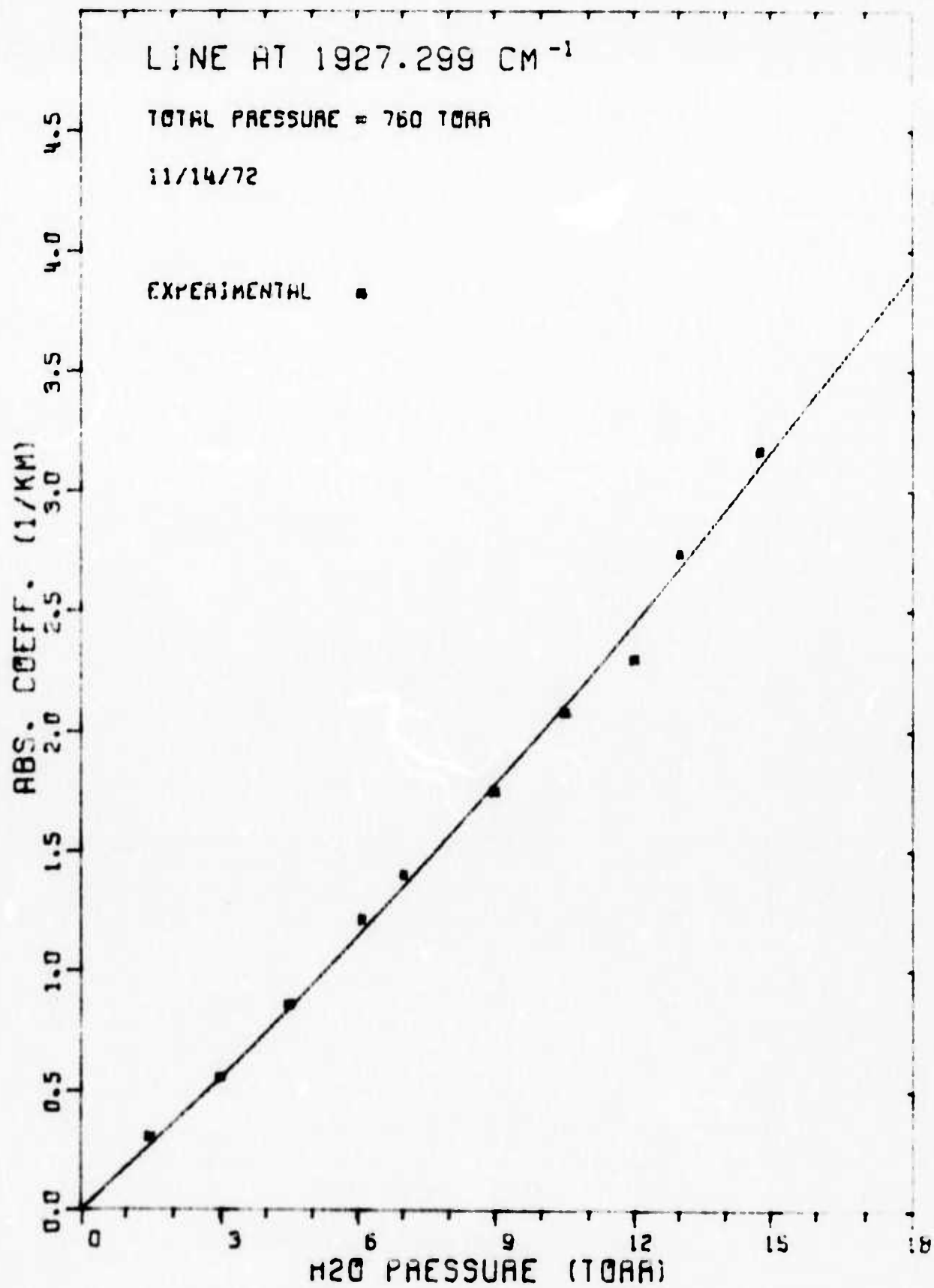
25

Fig. 15. Experimental data, 1931.409 cm^{-1}.
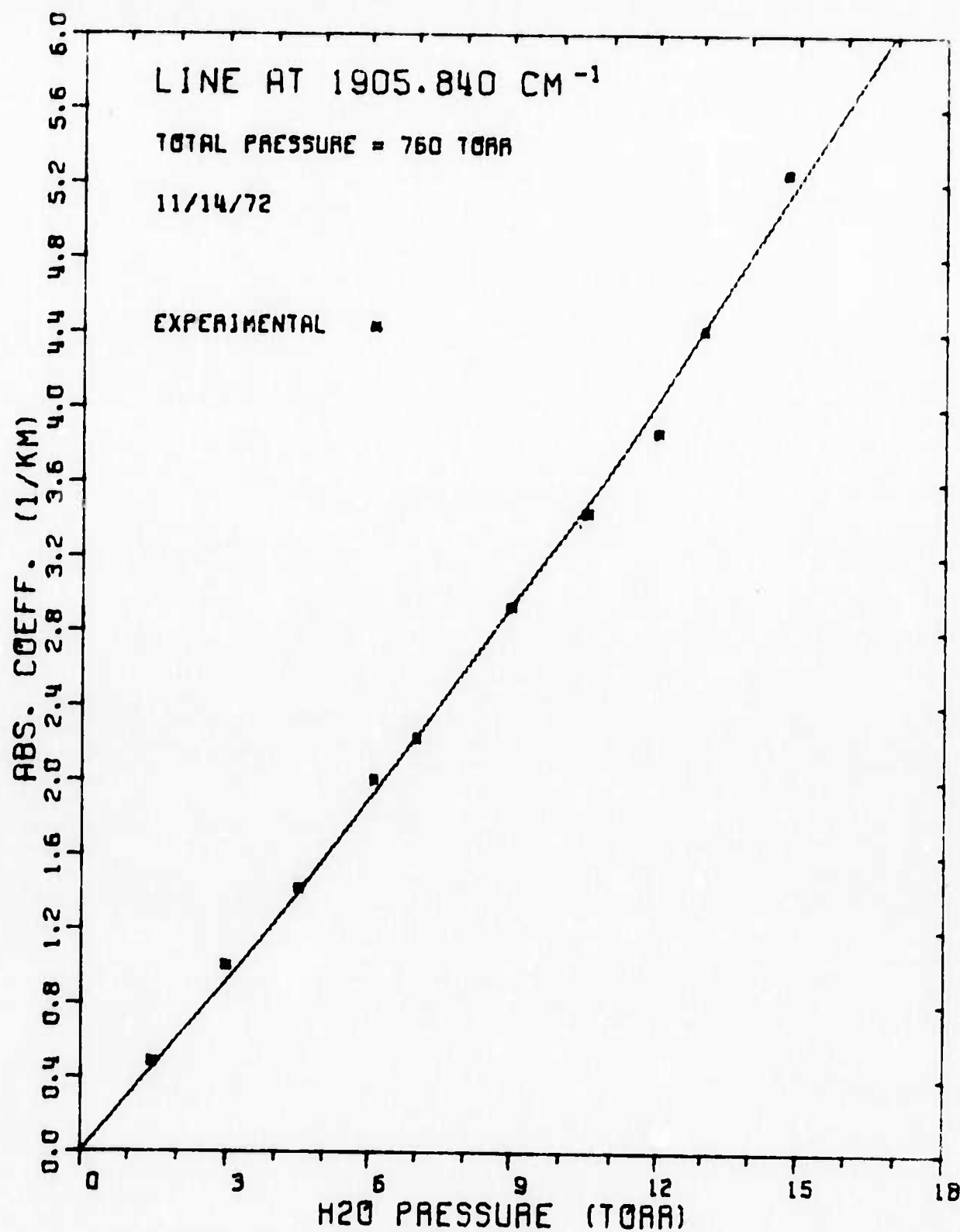
26

Fig. 16. Experimental data, 1927.295 cm^{-1}.
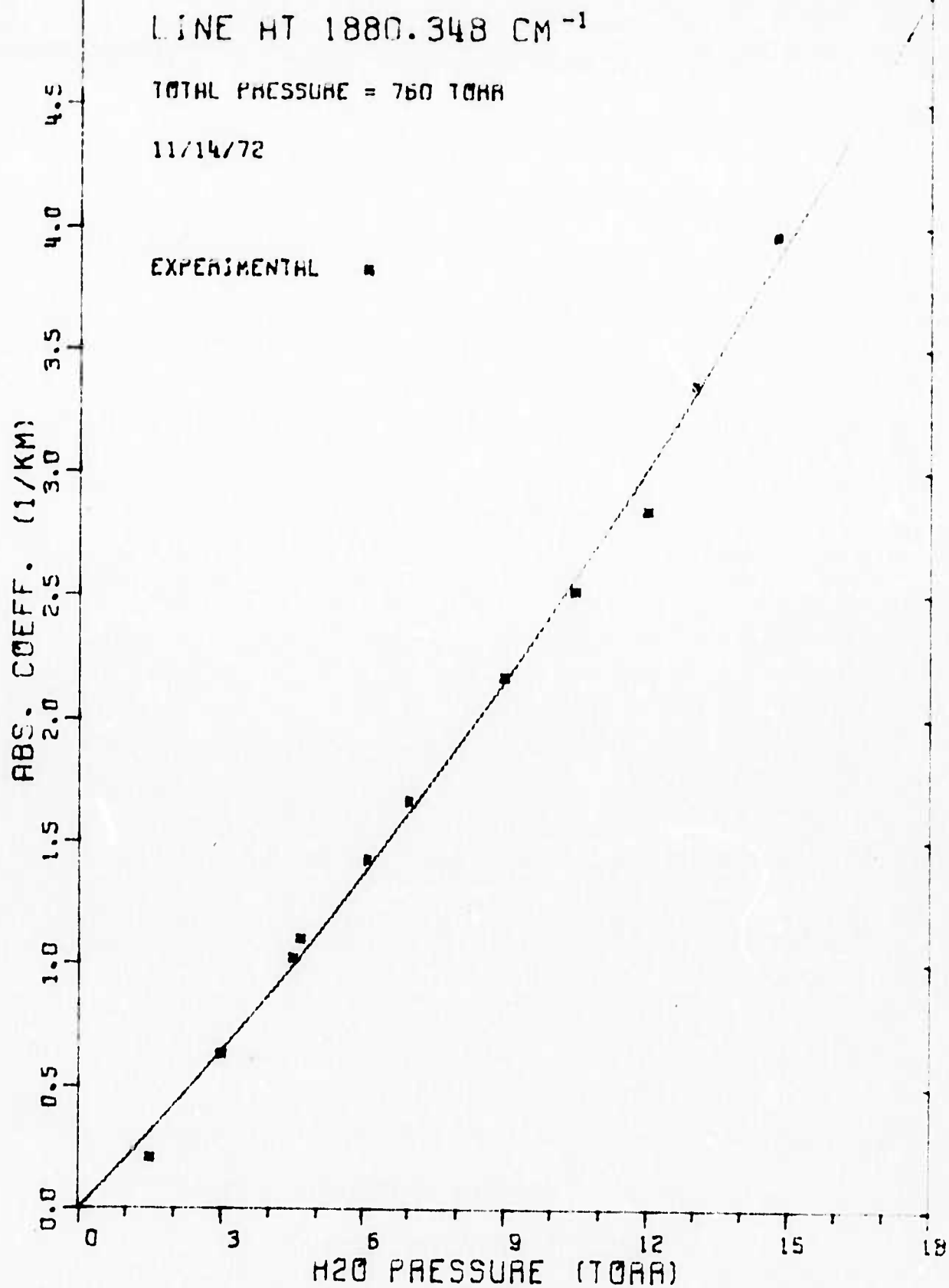
27

Fig. 17. Experimental data, 1905.840 cm^{-1}.

28

Fig. 18. Experimental data, 1880.348 cm^{-1}.

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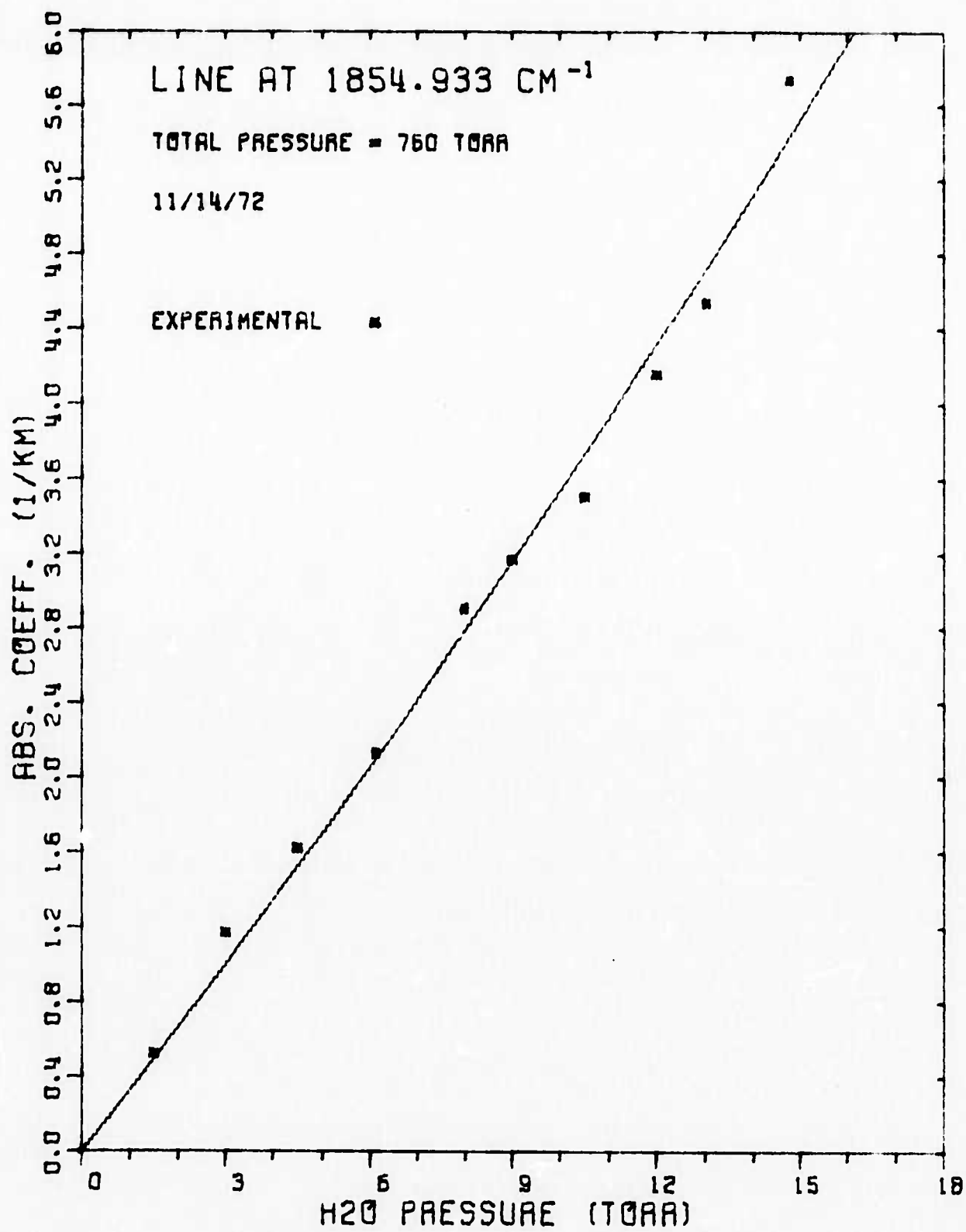
Fig. 19. Experimental data, 1854.933 cm⁻¹.

30

$$(2) \qquad k = \sum_i \frac{S_i^0 \; \alpha_i^0 \; p^2}{(\nu - \nu_0)^2} \qquad .$$

If the effective pressure of the H_2O-N_2 mixture is given as

$$(3) \qquad P_e = P + (B-1)p,$$

where B is the self-broadening coefficient, then

$$(4) \qquad k = \text{constant} \times p \; [P + (B-1)p]$$

or

$$(5) \qquad k = bp + cp^2.$$

Thus, for P = 760

$$(6) \qquad B = 1 + 760 \; c/b.$$

This method was used to compute a broadening coefficient from the experimental data for each laser line. The results are tabulated in column two of Table IV. In the earlier calculations, given in Section III, a value of B=5 was used, after Calfee[14]. As can be seen the experimental values vary from 7.6 to 26.6 neglecting the negative value obtained for 1957.051 cm^{-1}. We have concluded that 1957.051 does not fit the theoretical model. In fact, as will be seen in plots to be presented in the next section of this report, this laser line lies within the half-width of a rather strong water vapor line.

Table V gives the empirical equations for the absorption coefficient expressed in the form of Eq. (4). These equations can be used to obtain the coefficients for total pressures other than 760 torr also. The result may be compared with the experimental values at lower pressure as given in 3271-4. Recall that these equations are only alternative forms of the experimental data of Figs. 9-19 and thus apply only at 74°F. As noted above the equation for 1957.051 appears odd with a negative "B" but nevertheless this equation is a correct expression for the absorption coefficient at this frequency.

31

TABLE IV

Comparison of measured and curve fit (bx + cx²) values of absorption coefficients for 11 CO lines and 13 water vapor pressures at 760 torr total pressure and 74°F. Path lengths used in experiment noted, see text for discussion of experimental broadening coefficients.

WAVENUMBER cm⁻¹	EXP 8	1.5 TORR .732 km K 1/KM	KFIT 1/KM	3.0 .732 K	KFIT	4.5 .732 K	KFIT	4.5 .732 K	KFIT	4.65 .366 K	KFIT	6.1 .366 K	KFIT	7.0 .732 K	KFIT	8.0 .366 K	KFIT	9.0 .366 K	KFIT	10.5 .732 K	KFIT	12.0 .732 K	KFIT	13.0 .732 K	KFIT	15.75 .366 K	KFIT
1854.933	7.6	.524	.496	1.17	1.00	1.62	1.53					2.13	2.10			2.91	2.79	3.18	3.17	3.51	3.74	4.16	4.32	4.54	4.72	5.72	6.41
1880.348	16.1	.205	.313	.635	.645	1.02	.995			1.10	1.03	1.43	1.39	1.67	1.62			2.17	2.15	2.52	2.57	2.84	3.02	3.35	3.32	3.97	3.88
1905.841	9.9	.484	.451	1.00	.917	1.42	1.40					2.01	1.93	2.23	2.24			2.94	2.94	3.44	3.48	3.87	4.04	4.41	4.43	5.25	5.12
1927.299	10.4	.301	.272	.555	.553	.862	.845					1.22	1.17	1.40	1.35	1.23	1.12	1.75	1.78	2.08	2.11	2.30	2.45	2.74	2.68	3.10	3.10
1931.409	8.2	.181	.199	.376	.403	.593	.613	.655	.613			.883	.843	.964	.975			1.26	1.28	1.46	1.51	1.62	1.75	1.92	1.91	2.27	2.70
1948.729	13.3	.193	.230	.482	.471	.744	.722					1.04	1.00	1.17	1.17			1.58	1.54	1.81	1.84	2.01	2.14	2.39	2.35	2.75	2.72
1952.907	15.2	.077	.123	.218	.252	.357	.389			.51	.403	.536	.541	.617	.631			.883	.838	1.02	1.00	1.07	1.17	1.29	1.29	1.52	1.50
1957.051	-3.6	.556	.556	1.10	1.10	1.51	1.64			1.68	1.69	2.66	2.20	2.43	2.51			3.09	3.19	3.62	3.68	3.99	4.17	4.52	4.49	5.16	5.24
1970.129	13.6	.251	.197			.643	.618			.74	.64	.877	.859	.886	.999			1.37	1.32	1.51	1.58	1.74	1.84	2.1	2.02	2.38	1.34
1974.374	26.6	.035	.058	.057	.123	.165	.192	.248	.192	.256	.177	.283	.273	.336	.321			.458	.435	.538	.527	.561	.625	.715	.693	.82	.821
1978.586	21.5	.019	.053	.034	.110	.129	.171					.282	.24	.269	.287	.387	.329	.395	.379	.424	.456	.459	.538	.599	.594	.56	.700

32

TABLE V

EMPIRICAL EQUATIONS FOR THE ABSORPTION
COEFFICIENTS AT 11 CO LASER WAVELENGTHS

1854.933	$k = 4.29 \times 10^{-4} p(760 + 6.6p)$
1880.348	$k = 2.67 \times 10^{-4} p(760 + 15.1p)$
1905.840	$k = 3.89 \times 10^{-4} p(760 + 8.9p)$
1927.299	$k = 2.34 \times 10^{-4} p(760 + 9.4p)$
1931.409	$k = 1.72 \times 10^{-4} p(760 + 7.2p)$
1948.729	$k = 1.97 \times 10^{-4} p(760 + 12.3p)$
1952.907	$k = 1.05 \times 10^{-4} p(760 + 14.2p)$
1957.050	$k = 4.93 \times 10^{-4} p(760 - 4.6p)$
1970.129	$k = 1.68 \times 10^{-4} p(760 + 12.6p)$
1974.374	$k = 4.88 \times 10^{-5} p(760 + 25.6p)$
1978.586	$k = 4.45 \times 10^{-5} p(760 + 20.5p)$

VI. COMPARISON OF MEASUREMENTS AND CALCULATIONS

In 1967 W.S. Benedict and R.F. Calfee published tables of
water vapor line strengths, positions, half-widths, and lower energy
levels for the 6.3μ water vapor band[1]. Several workers have recently
used these data tables to predict transmittance at CO laser fre-
quencies[15,16,17]. These workers have used an absorption coefficient
subroutine (ABSCOE) based on the Lorentz line shape originally written
by Calfee and Deutschman[14]. The equations used have been reviewed
in reference [11] and Section III of this report, see Eq. (1).

In addition to the tabulated data there are four parameters
which must be selected. Following the work of Calfee and later of
McClatchey, "accepted" or generally used values for these parameters
have evolved. The first constant is B, the self-broadening coefficient.
An average value of 5 for water vapor has been most generally used.
BX is the exponent of a temperature term in the line strength versus
temperature dependence. For H_2O, BX = 1.5. CX is the exponent in
the temperature dependence of half-width. An average empirical
value of 0.62 for H_2O has been used. Finally when computing at
frequency ν, effects from (ν-BOUND) to (ν+BOUND) are included. A
value of 25 cm^{-1} has been used for BOUND. Ford[18] has shown that
significant changes occur until BOUND is increased to 150 cm^{-1}.

McClatchey[19] has contended that due to lack of precise knowledge of the line shape one is deceiving himself if a BOUND greater than 25 cm^{-1} is used, a view with which we are in essential agreement.

Using the above procedure the absorption coefficients for the eleven CO laser lines were computed. These results are given in Figs. 20-30 for the eleven lines and are marked "Lorentz" on the plots. The experimental data from Figs. 9-19 is also repeated for comparison. The computed absorption coefficients are always lower than the experimental values. Column four of Table VI gives the

<div align="center">

TABLE VI
COMPARISON AT 12 TORR WATER VAPOR OF EXPERIMENTAL
AND CALCULATED ABSORPTION COEFFICIENTS

p = 12 TORR   P = 760 TORR

</div>

LINE cm^{-1}	k_{exp} km^{-1}	$k_{LORENTZ}$ km^{-1}	$\left(\dfrac{exp-LOR}{exp}\right)$	k_{OSU} (1.77, 3)	$\left(\dfrac{exp-OSU}{exp}\right)$
1854.933	4.32	2.10	0.514	4.29	0.00694
1880.348	3.02	1.72	0.43	3.34	-0.106
1905.841	4.04	2.37	0.413	3.92	0.0297
1927.299	2.45	1.43	0.416	2.74	-0.118
1931.409	1.75	0.909	0.481	1.74	0.0057
1948.729	2.14	1.624	0.24	2.66	-0.243
1952.907	1.17	0.61	0.479	1.20	-0.0256
1957.051	4.17	3.03	0.27	3.36	0.194
1970.129	1.84	1.33	0.277	2.14	-0.163
1974.374	0.625	0.276	0.558	0.629	-0.0064
1978.586	0.538	0.182	0.66	0.440	-0.182

percent difference between the experimental and "Lorentz" values at a water vapor partial pressure of 12 torr. Figures 20-30 also include expanded versions of Figs. 4, 5, and 6 in the regions of the eleven CO laser lines. If the distance from the center of the nearest strong water vapor line is compared to the percent difference from Table VI, the results fall roughly into two groups with the largest percent difference occurring for the frequencies that are far from a water

<div align="center">34</div>
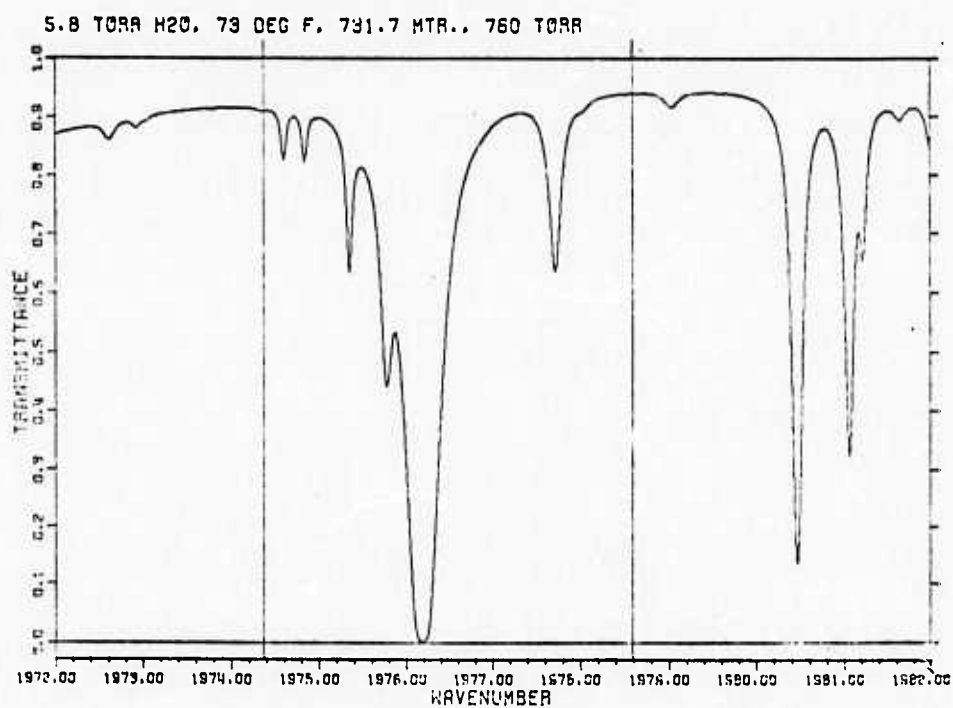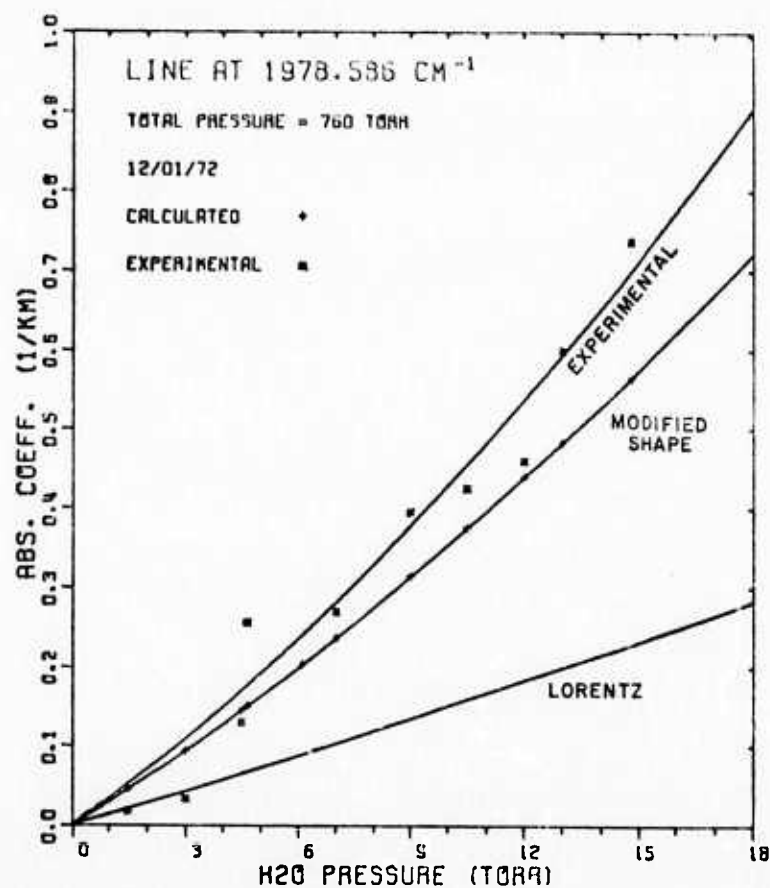
Fig. 20. Comparison of experimental data and theoretical
calculations - 1978.586 cm⁻¹.

35
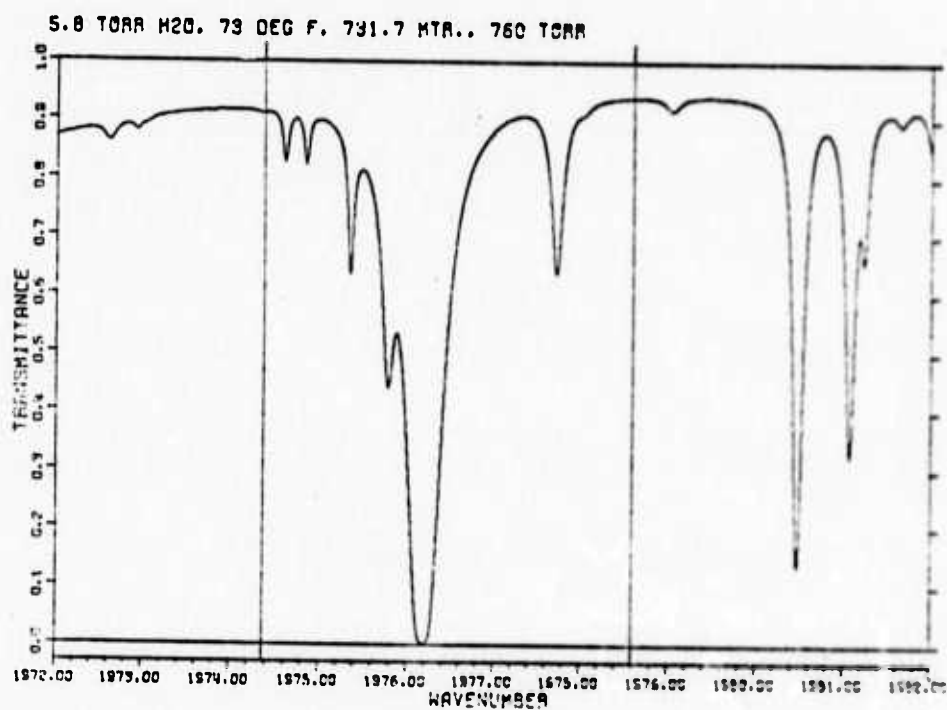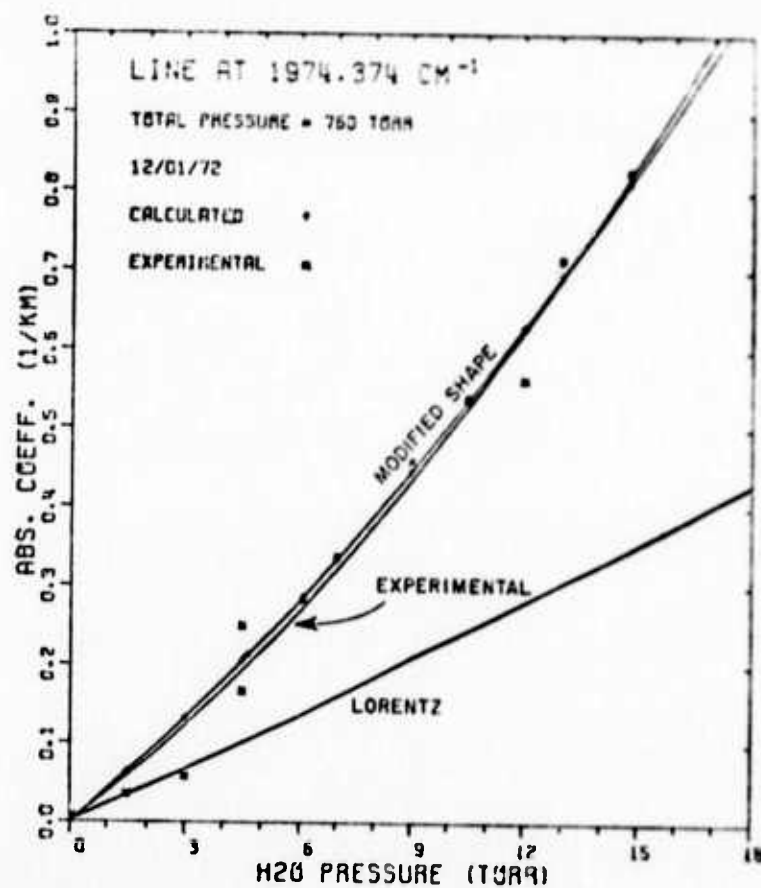
Fig. 21. Comparison of experimental data and theoretical
calculations - 1974.586 cm^{-1}.
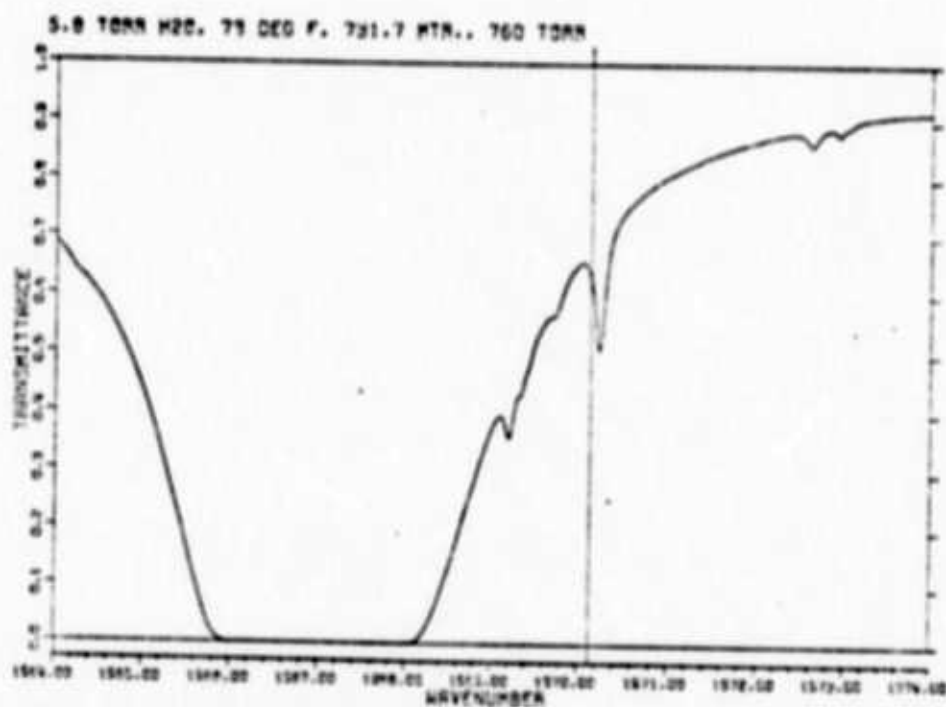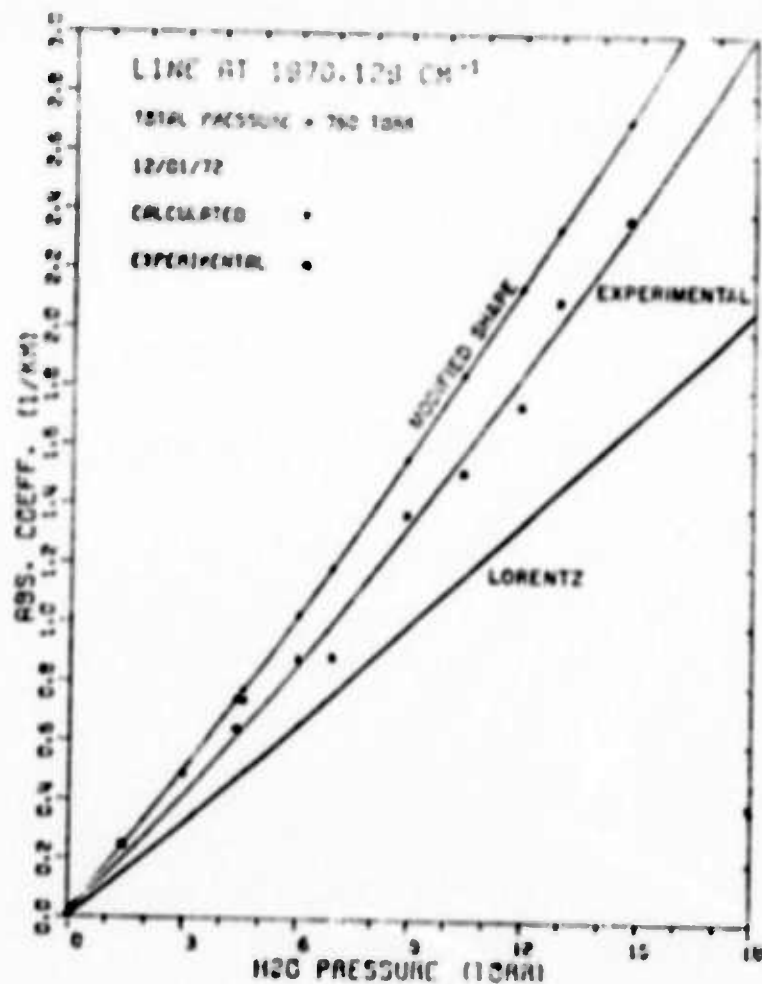
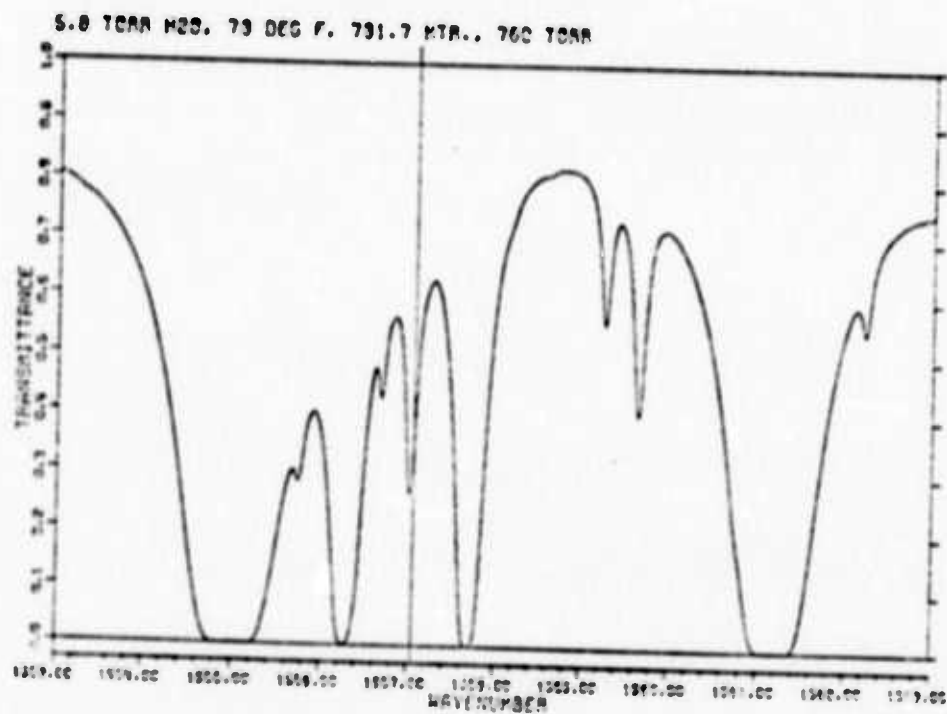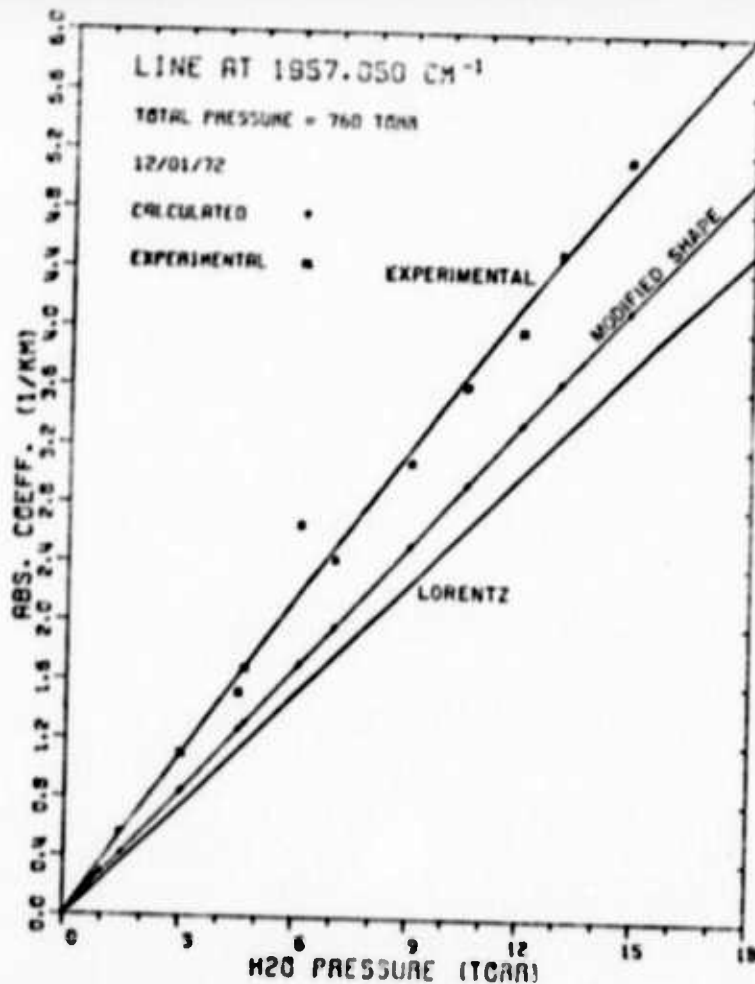Fig. 22. Comparison of experimental data and theoretical calculations - 1970.125 cm⁻¹.

Fig. 23. Comparison of experimental data and theoretical calculations - 1957.050 cm⁻¹.

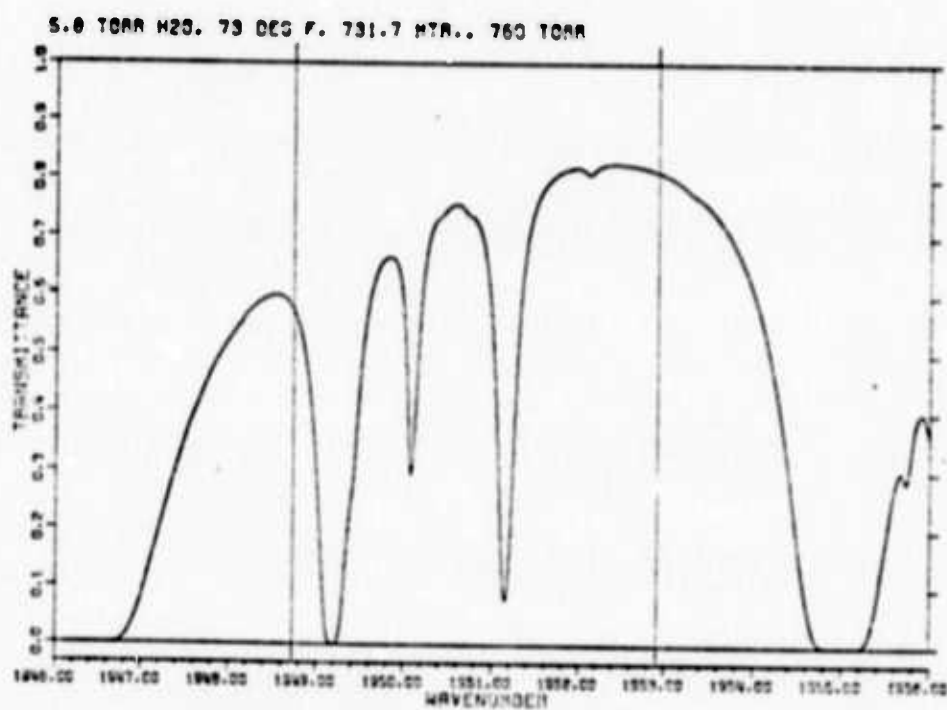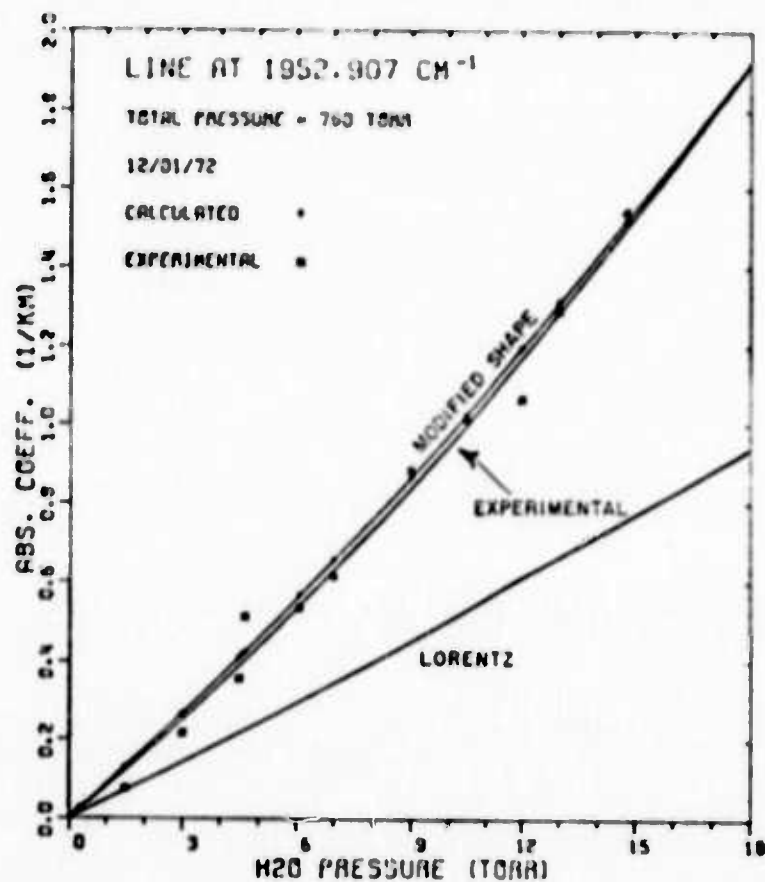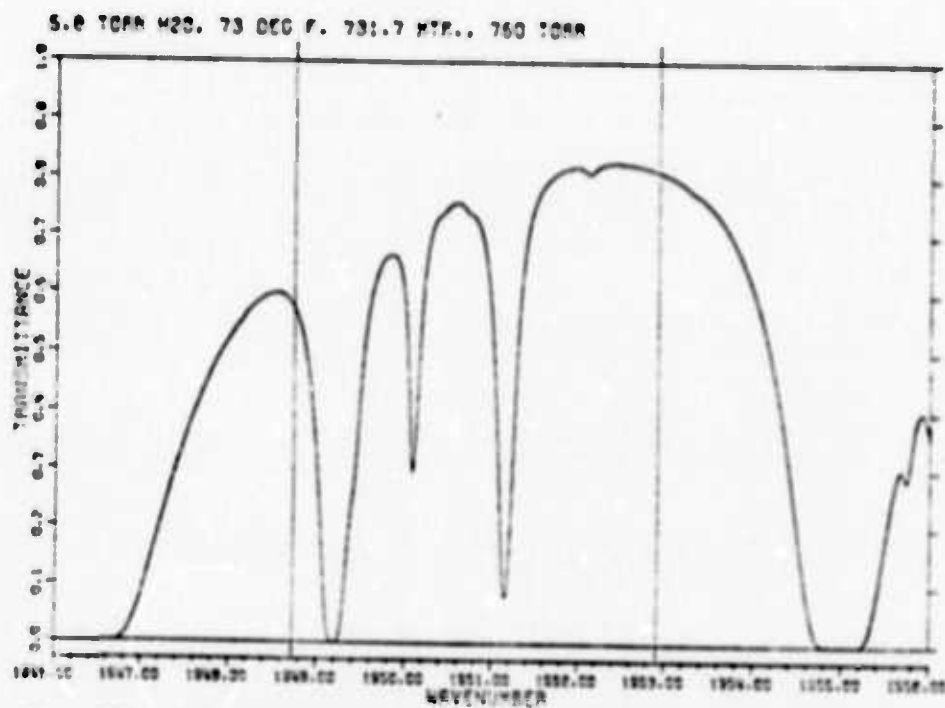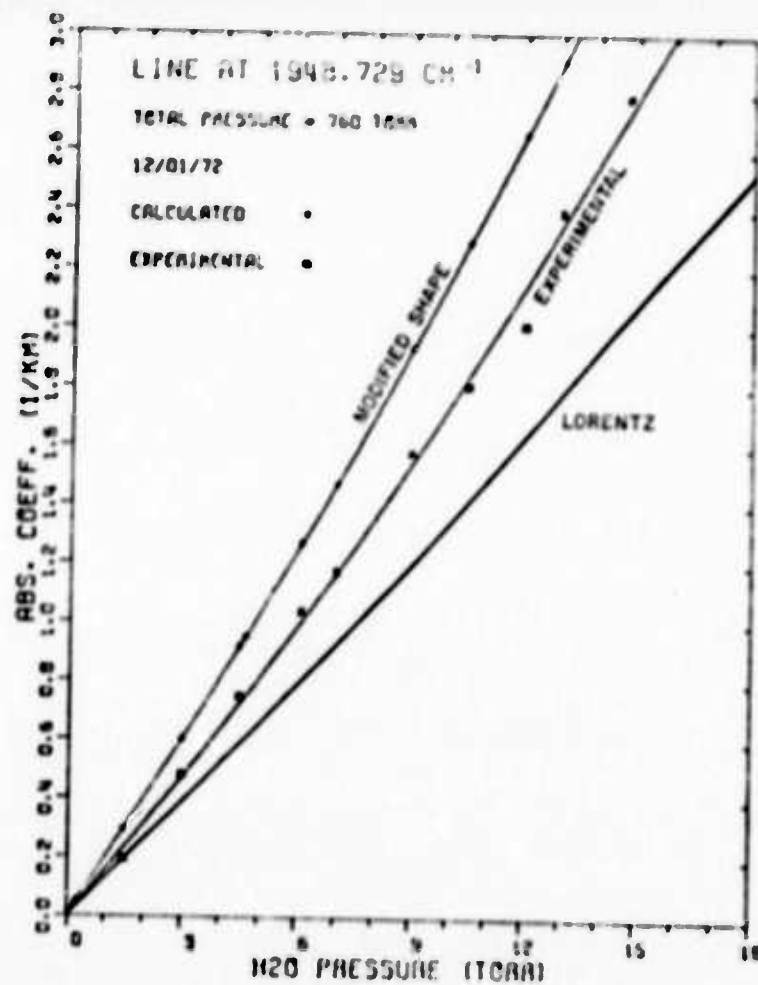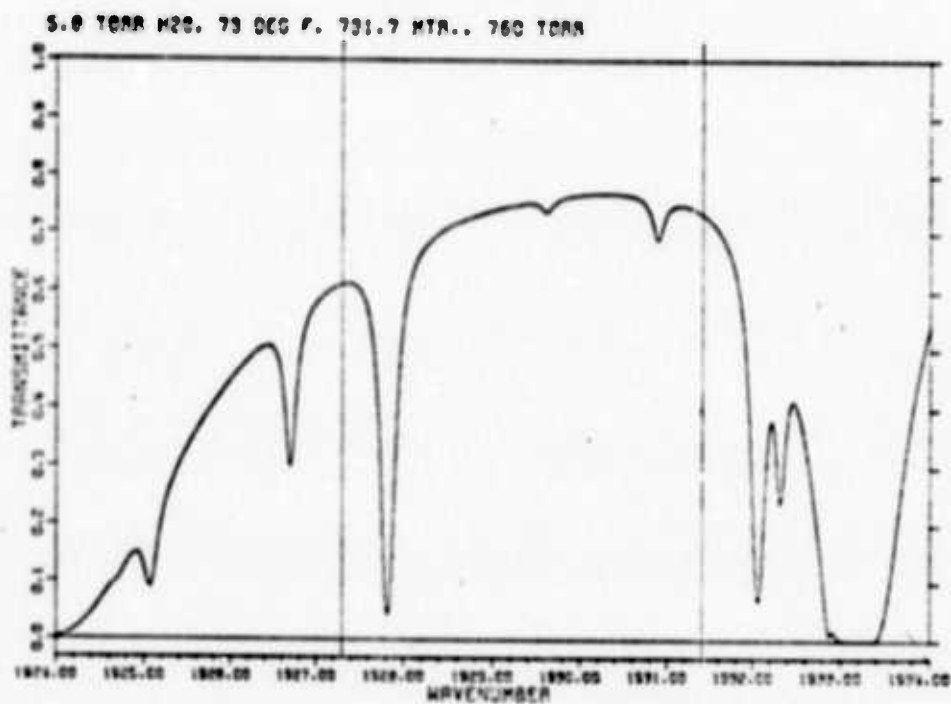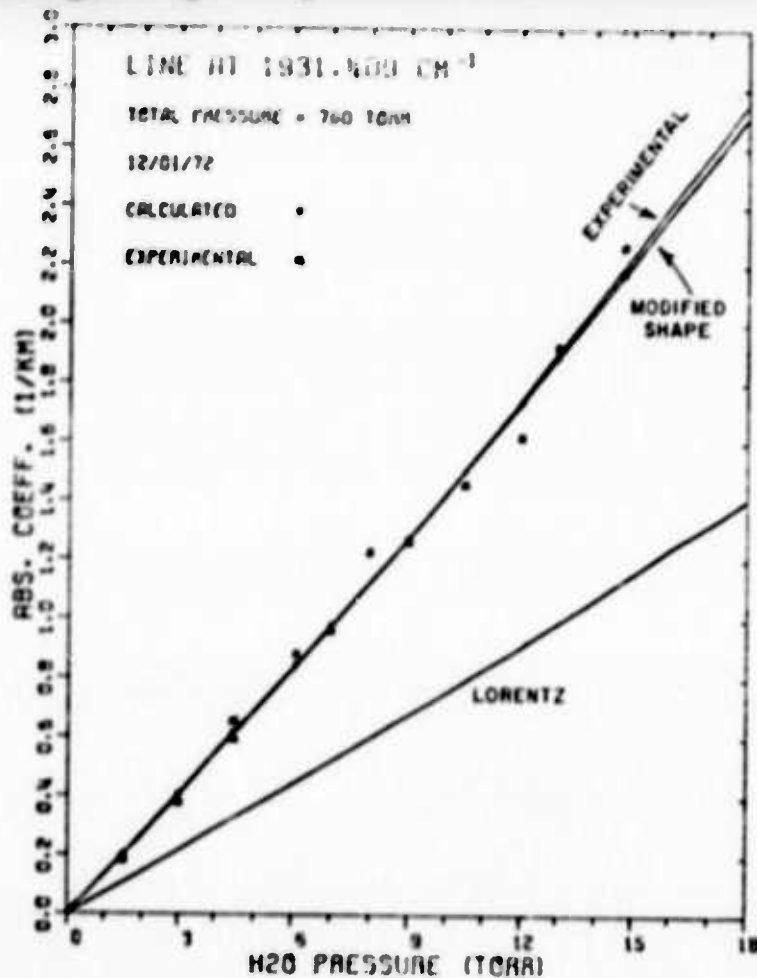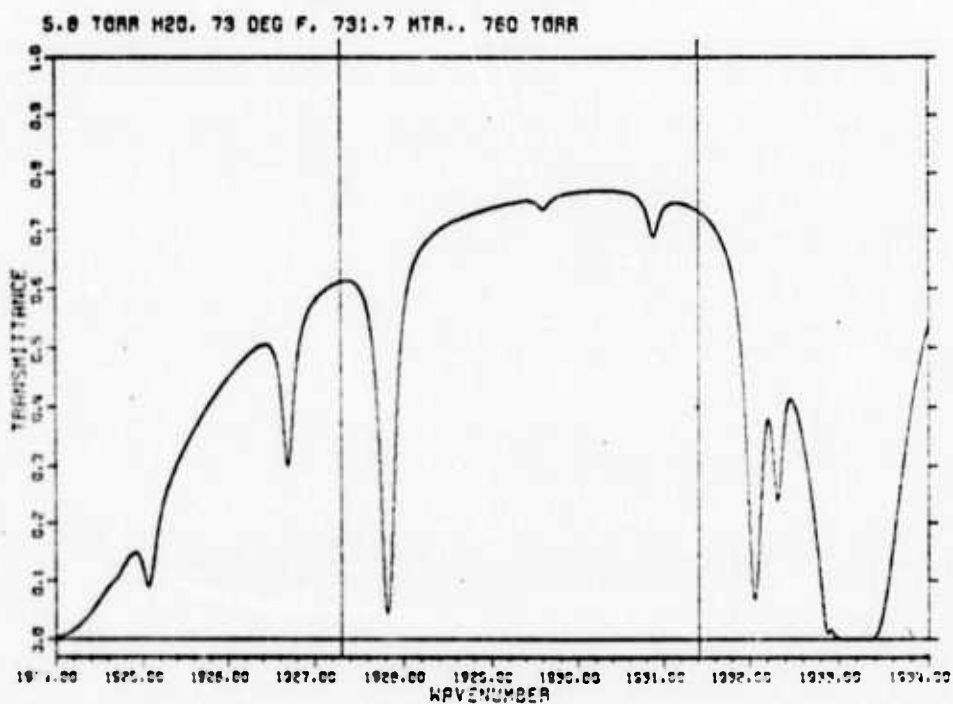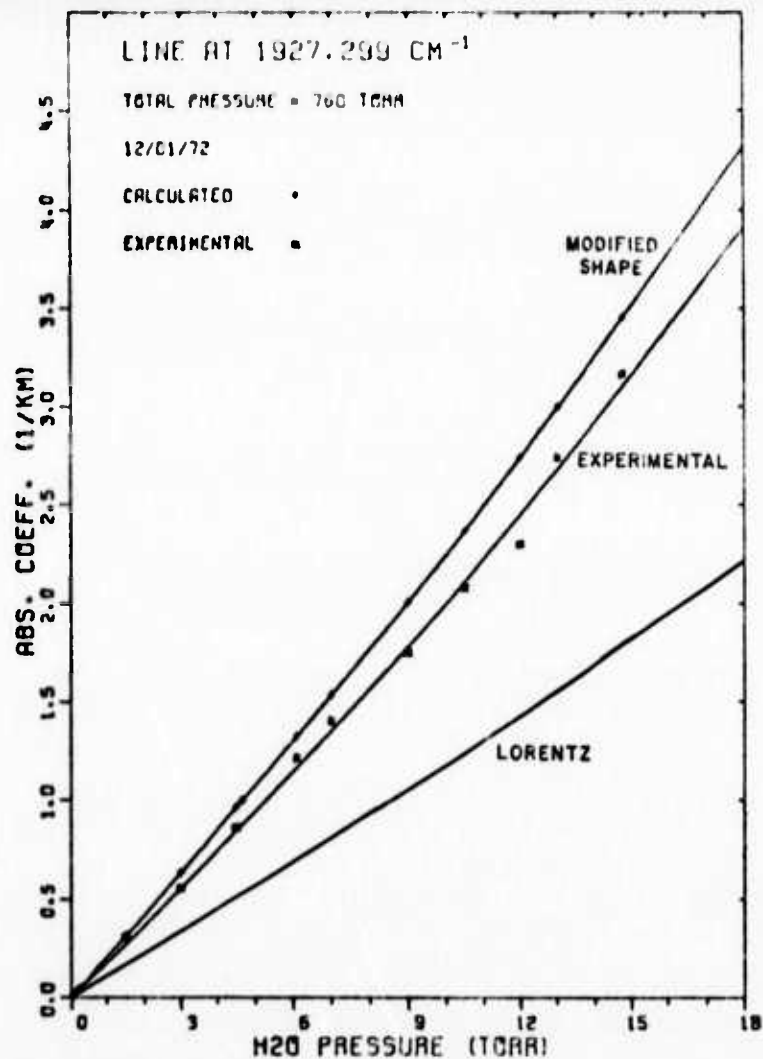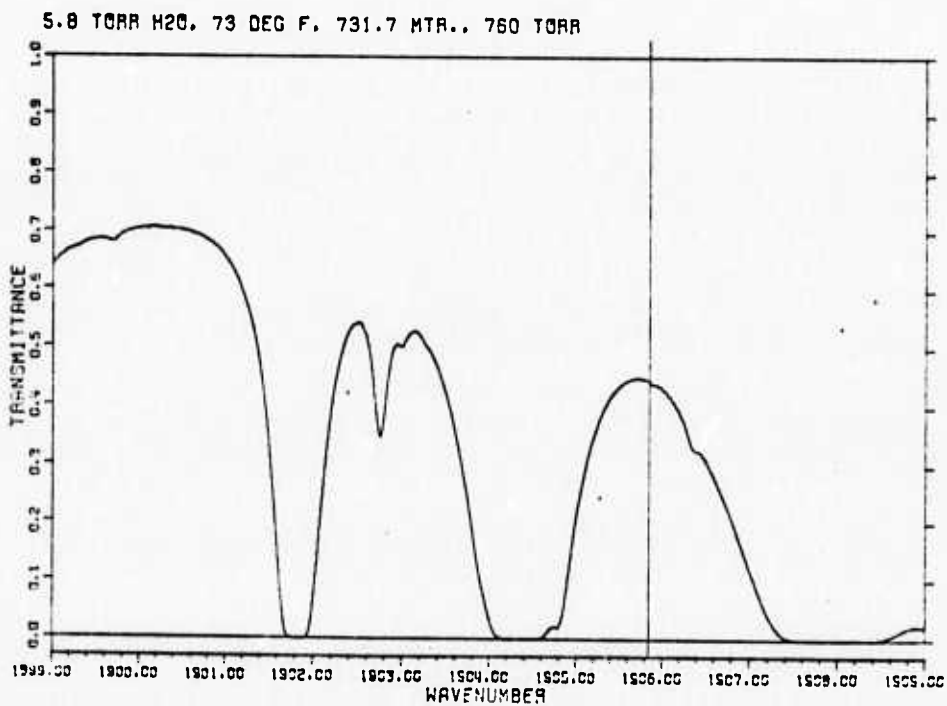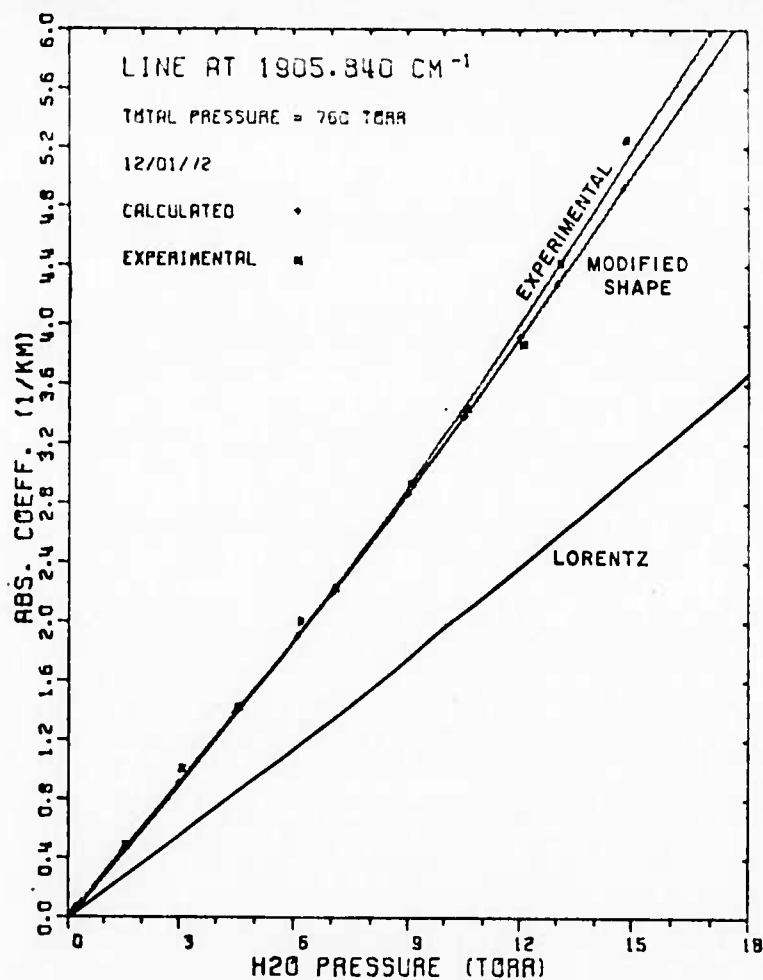Fig. 24. Comparison of experimental data and theoretical calculations - 1952.907 cm⁻¹.

39

Fig. 25. Comparison of experimental data and theoretical calculations - 1948.729 cm^{-1}.

Fig. 26.   Comparison of experimental data and theoretical
calculations - 1931.409 cm^{-1}.

41

Fig. 27. Comparison of experimental data and theoretical
calculations - 1927.299 cm⁻¹.

42

Fig. 28. Comparison of experimental data and theoretical
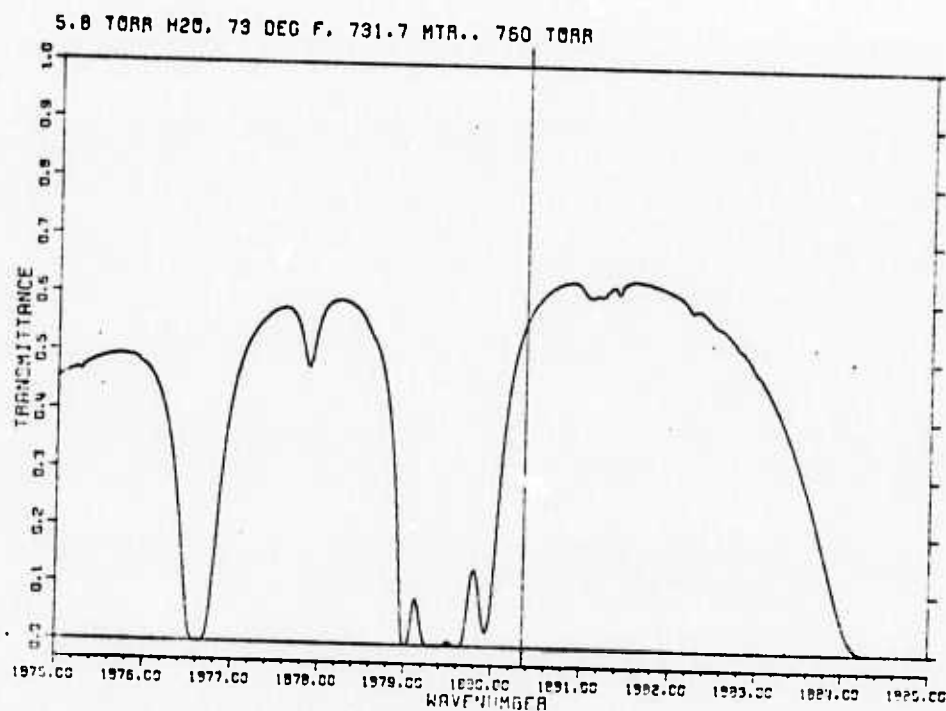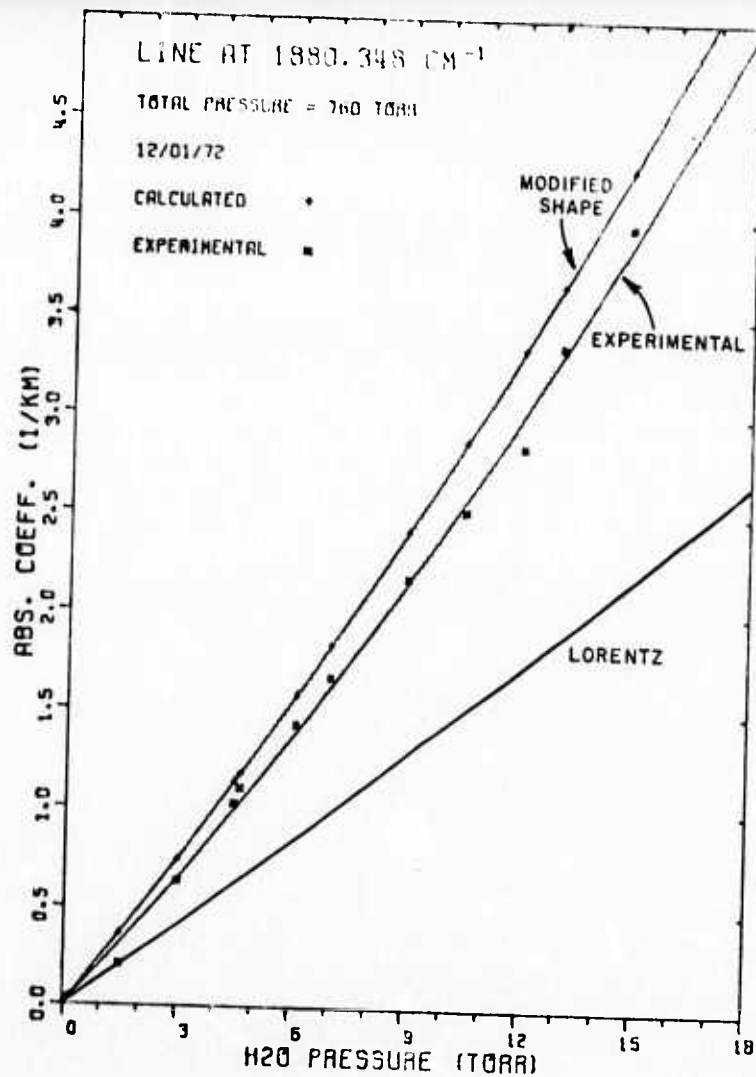calculations - 1905.840 cm⁻¹.

43

Fig. 29. Comparison of experimental data and theoretical
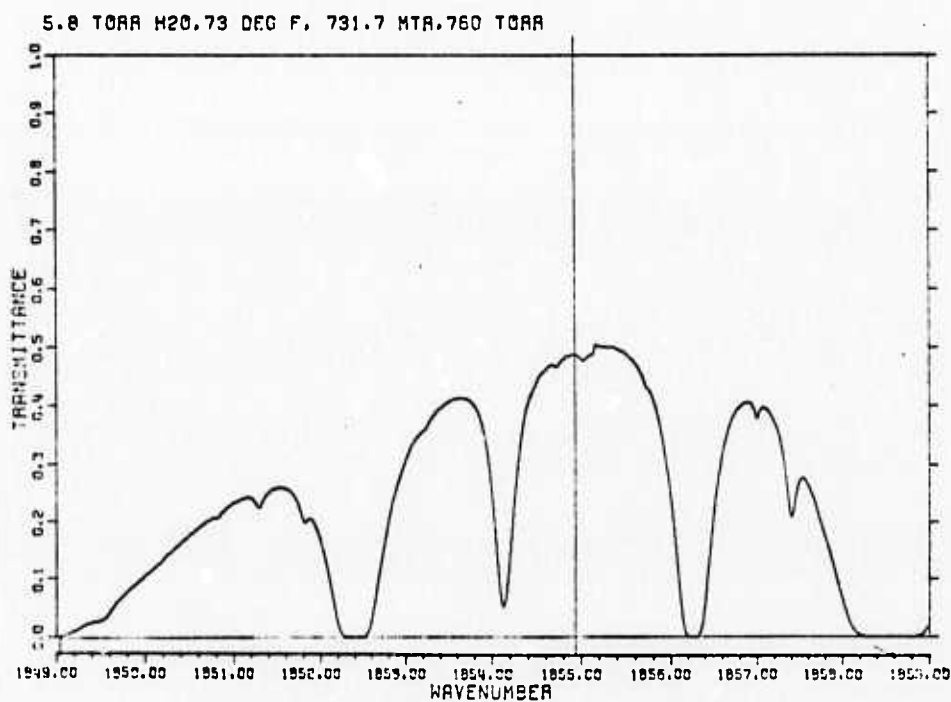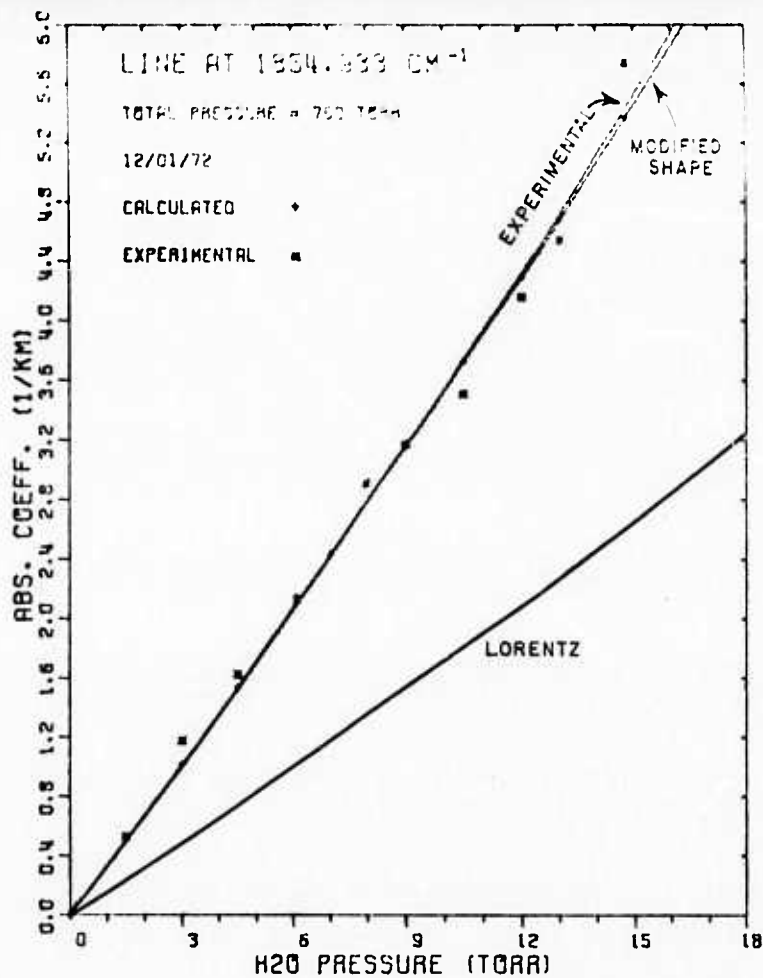calculations - 1880.348 cm-1.

44

Fig. 30. Comparison of experimental data and theoretical calculations - 1854.933 cm^{-1}.

vapor line. The calculated results appear to be most in error when a summation of the far wings of water vapor lines is dominant. This leads to the conclusion that, although errors in the data table entries may be also important, by far the greatest problem is that the Lorentz line shape does not correctly describe the true shape especially far from the line center.

It is interesting to compare the experimental results with theoretical calulations made using different line shapes. Two different line shapes were used. The first already discussed is the familiar Lorentz shape

$$k_\nu = \frac{S\alpha}{\pi[(\nu-\nu_0)^2 + \alpha^2]} \quad .$$

The second shape was one derived by one of us (Trusty). It is similar to an earlier form suggested by Benedict[2]. In our case, however, the pair of equations are designed so that they give the same value for k_ν at the transition frequency located ν_m wavenumbers from the line center. The equations are

$$k_a = \frac{C\,S\,\alpha}{\pi[(\nu-\nu_0)^2 + \alpha^2]} \quad , \quad 0 \leq |\nu-\nu_0| \leq \nu_m$$

and

$$k_b = \frac{C\,S\,\alpha\,\nu_m^n}{\pi[\nu_m^2 + \alpha^2](\nu-\nu_0)^n} \quad , \quad |\nu-\nu_0| \geq \nu_m,$$

with the normalization constant given by

$$C = \frac{S}{2\displaystyle\int_0^{\nu_m} k_a + \int_{\nu_m}^{\omega} k_b} \quad .$$

We used the following procedure to arrive at values for ν_m and n. An interactive computer program was written wherein ν_m and n could be varied and the absorption coefficient (summation value) calculated. BOUND was still set at 25 cm^{-1}. The frequency of one of the eleven CO laser lines was selected (1952.907 cm^{-1}). The self broadening coefficient was taken to be the experimental value of 15.2 from Table IV. A water vapor pressure of 12 torr was selected and the computed absorption coefficient was compared with the experimental

46

value (KFIT) for 12 torr from Table IV. The computed coefficient was found to be much more sensitive to the value of n than to the location ν_m. This is evident from the contour plot of the line shape function, see Fig. 31. Best agreement was found when ν_m was set equal to three half widths and n had a value of 1.77. In Figs. 32, 33, and 34 the resulting line shape is compared with the Lorentz shape.

With ν_m = 3 and n = 1.77 the absorption coefficients were now computed for all eleven CO laser lines and for all partial pressures of water vapor up to 18 torr using the experimental β's for each line. These results are presented in Figs. 20-30 and labeled "MODIFIED SHAPE". Also in Table V the calculated results are compared with experimental values at one water vapor pressure (12 torr).

VII.   CONCLUSIONS

Accurate measurements of absorption coefficients at CO laser frequencies are required in order to evaluate the importance of propagation loss in various systems applications. This report and Report 3271-4 have presented the only accurate measurements of these parameters currently available. Careful attention to all phases of the laboratory experiments was required in order to achieve these results. In particular the measurement of the water content in a closed laboratory chamber must be undertaken with great care and numerous cross checks must be performed in order to avoid errors caused by inadequate mixing, condensation, adsorption, and inaccurate or unsuitable measuring equipment.

Accurate measurements of absorption coefficients are also necessary in order to guide theoretical developments in prediction by "synthetic spectra." This report has shown that in window regions near 5μ the experimental results are consistent with an enhanced wing line shape which is described.

Additonal measurements at other CO frequencies, and at HF and DF frequencies are underway at this laboratory. They are also expected to contribute to our overall understanding of the absorption problem and to further testing of the theoretical models.
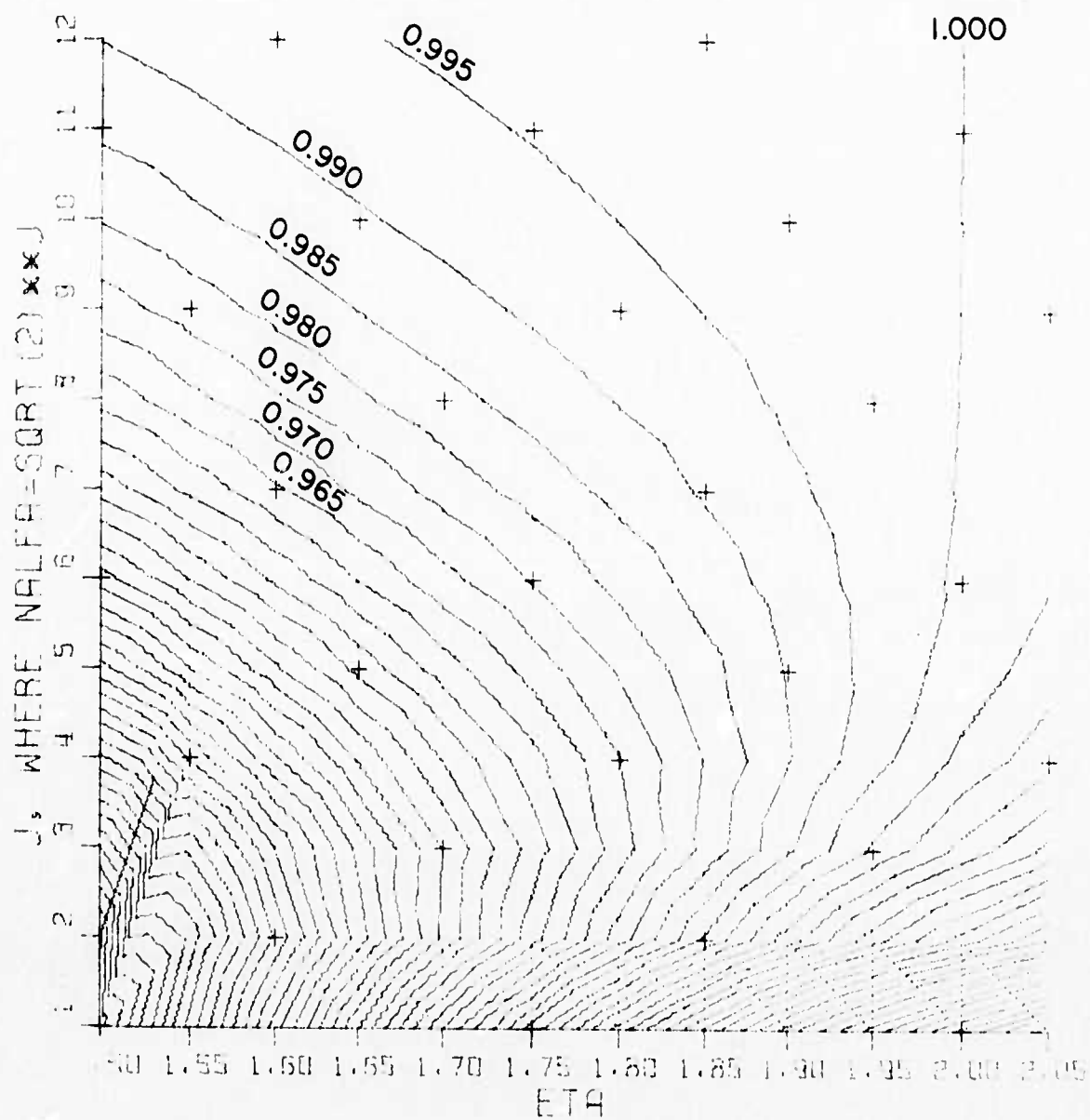
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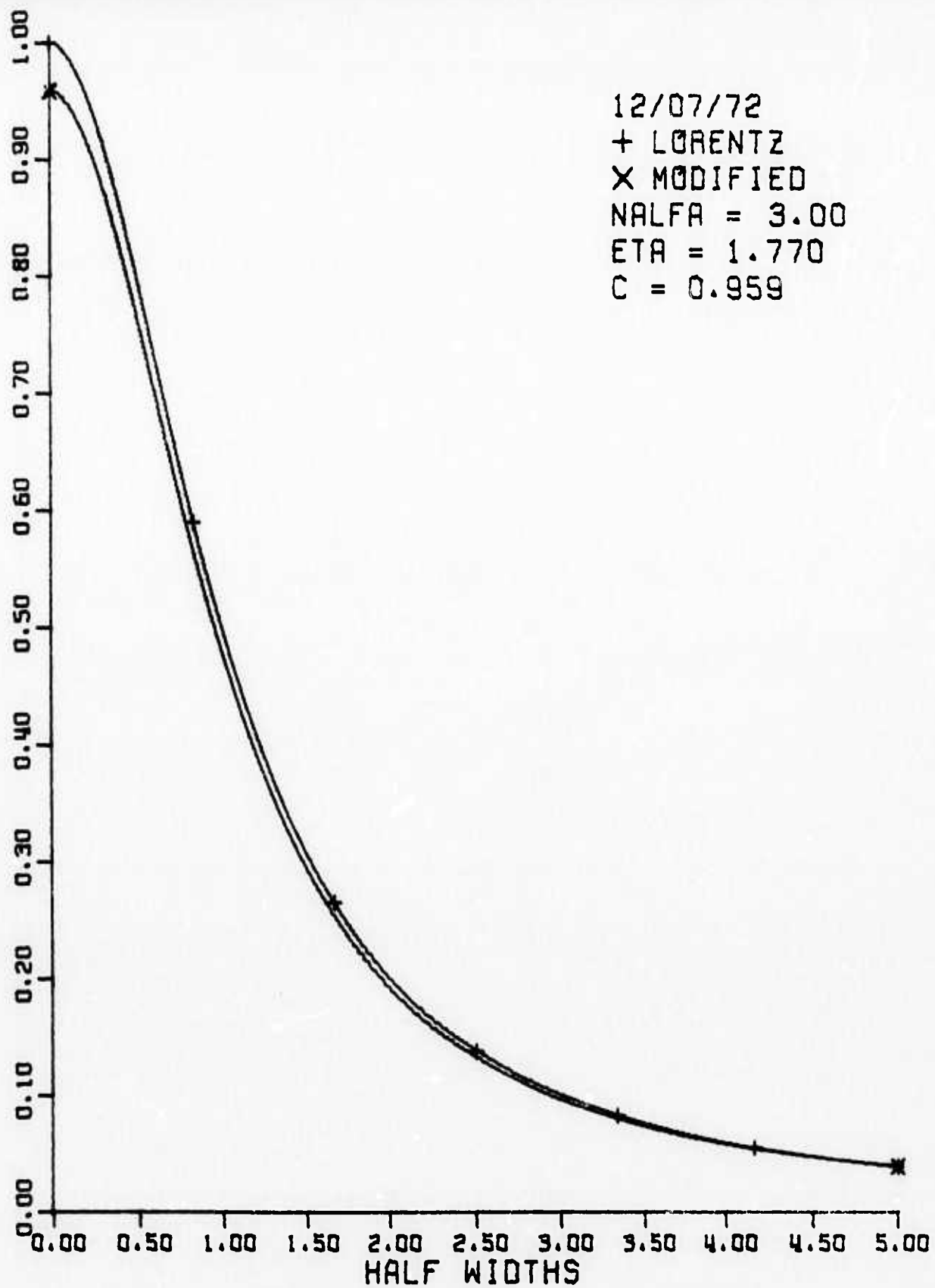Fig. 31. Contour plot of OSU modified line shape.

48

Fig. 32. Amplitude versus frequency for OSU modified
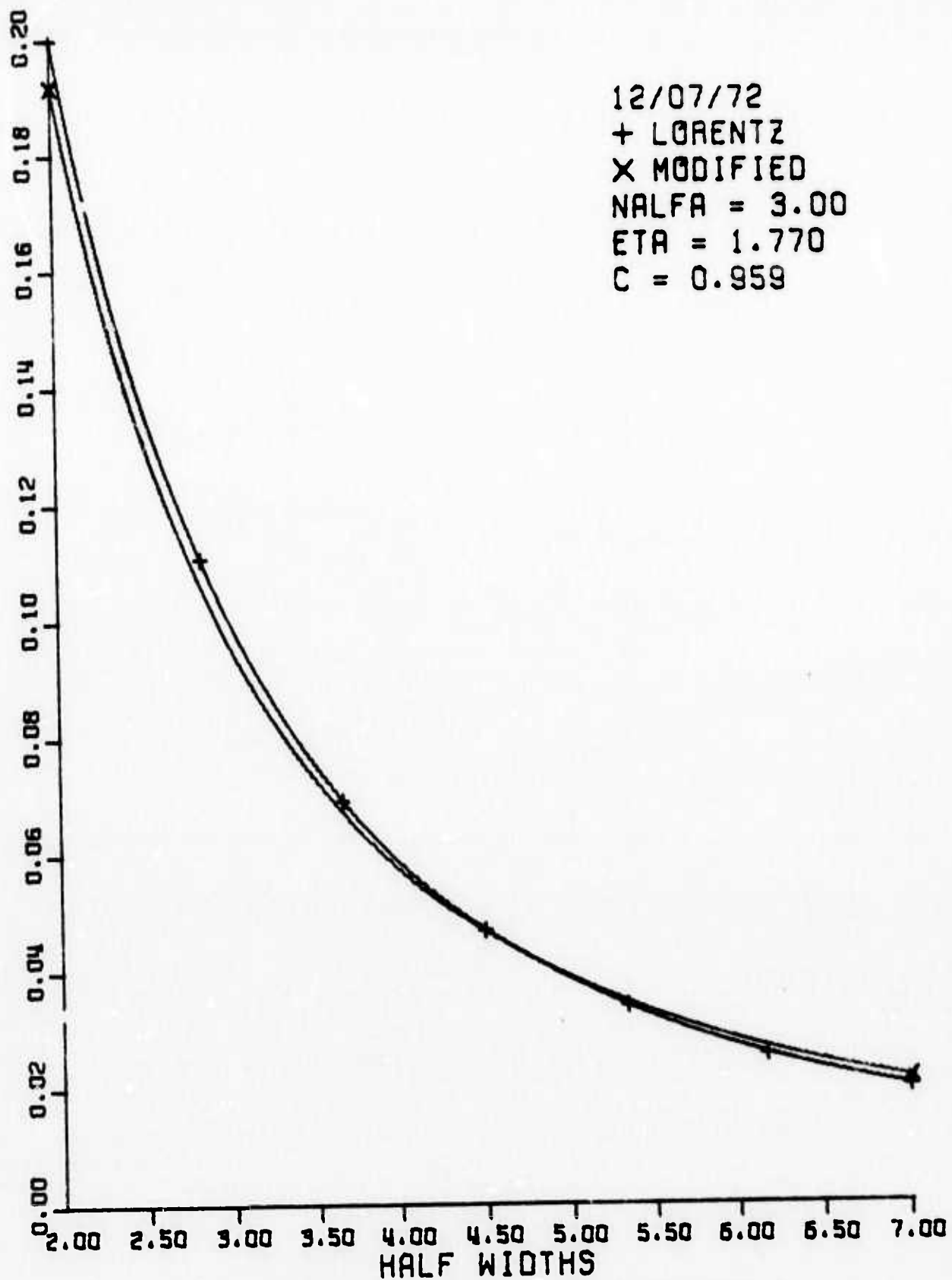line shape, 0-5 half-widths.

49

Fig. 33. Amplitude versus frequency for OSU modified
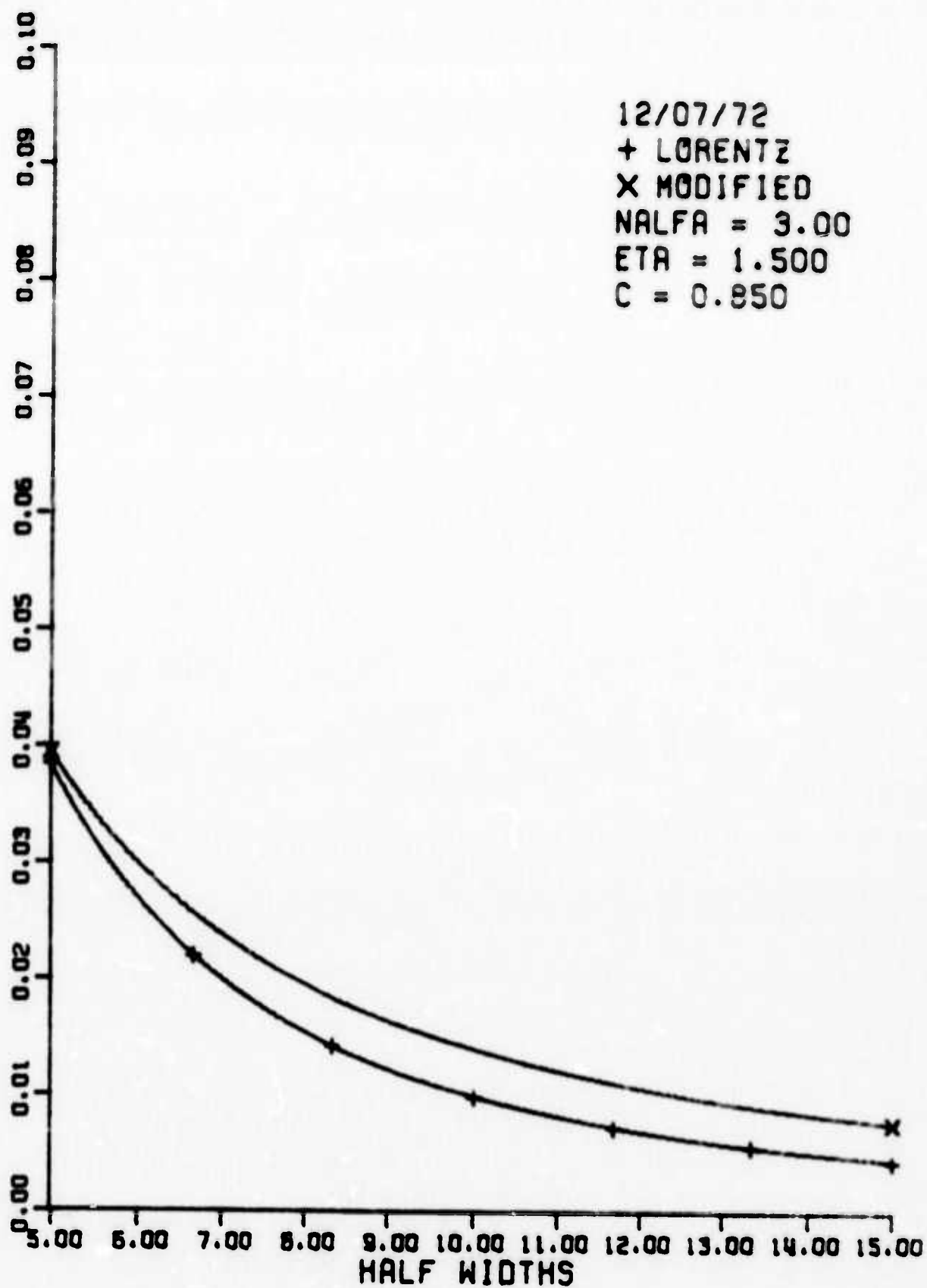line shape, 2-7 half widths.

50

Fig. 34. Amplitude versus frequency for OSU modified
line shape, 5-15 half widths.

51

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